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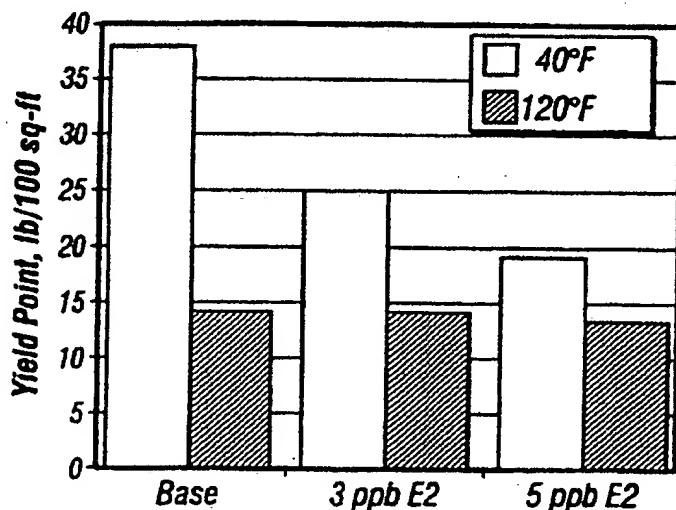
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(54) Title: THINNERS FOR INVERT EMULSIONS



(57) Abstract: A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said drilling fluids or well service fluids a thinner having the formula:  $R-(C_2H_5O)_n(C_3H_7O)_m(C_4H_9O)_k-H$  where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

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## THINNERS FOR INVERT EMULSIONS

### Background of the Invention

#### 1. Field of the Invention

5        This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids, at temperatures at or below about 50 degrees  
10   Fahrenheit (about 10 degrees Centigrade).

#### 2. Description of Relevant Art

      A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid  
15   include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

20        A drilling fluid typically comprises water and/or oil or synthetic oil or other synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in  
25   the fluid. Such dispersed water in oil is generally referred to as an invert emulsion or water-in-oil emulsion.

      A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or  
30   fluid-loss control agents, viscosifiers or viscosity control agents, and alkali. Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

5 An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

15 Thinner may be added to the drilling fluid or drilling mud systems before and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, problems with such prior art thinners may occur when using the drilling muds at low temperatures (temperatures at or below about 50°F (10° C)).

20 At such low temperatures, despite the use of known prior art thinners, oil based drilling fluids typically have high or increased viscosity, which may render the fluids unusable for drilling. After pumping into the wellbore, drilling fluids may undergo heating from the formation, depending on the depth of the wellbore and the temperature of the formation. For example, heating in the range of about 150° to about 250°F (about 66° to about 121°C) is not uncommon and subterranean temperatures as high as about 350°F (about 178°C), particularly in very deep wellbores, are known. The Arctic region, for example, is known to have very low surface temperatures but very high subterranean temperatures. Even more problematic are deepwater wells (i.e., typically wells below at least about 1500 feet), which subject drilling fluids to chilling from cold waters surrounding the riser as the fluid returns to the surface from the high temperature subterranean formation. Such chilling of oil

based drilling fluids typically increases their viscosity while such subterranean heating of oil based drilling fluids typically reduces their viscosity.

Preferably, thinners which reduce the viscosity of drilling fluids at low temperatures will not affect the viscosity of the fluids at high temperatures.

5 That is, in many cases, a thinner is desired that is capable of "selectively" influencing the rheology or particularly reducing the viscosity of oil-based drilling fluids only at lower temperatures, such as may be encountered at the ground surface of the wellbore, or in the riser surrounded by waters above a deepwater offshore well, for example.

10 Thinners and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore,  
15 such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are expected to be used in or to encounter low temperatures in drilling operations. As used herein, unless  
20 indicated otherwise, "low temperatures" shall be understood to mean temperatures at or below about 50°F (about 10°C).

### Summary of the Invention

25 According to the method of the present invention, a compound is added to a water-in-oil or invert emulsion drilling fluid or well service fluid which reduces the viscosity of the drilling fluid or well service fluid at low temperatures or which enables or enhances the ability of the drilling fluid or well service fluid to maintain its viscosity at low temperatures. The compound, which may be generally called a "thinner," continues to have this effect on a drilling fluid or  
30 well service fluid in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations. Further, this compound does not significantly affect the viscosity of the emulsion at high temperatures.

The compound has the following formula:



- 5 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

10 The invention also comprises the composition of a water-in-oil or invert emulsion drilling fluid or well service fluid containing this thinner compound.

#### **Brief Description of the Drawings**

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2 at different  
15 temperatures.

Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3 at different temperatures.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4 at different  
20 temperatures.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5 at different temperatures.

25 Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6 at different temperatures.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7 at different  
30 temperatures.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8 at different temperatures.



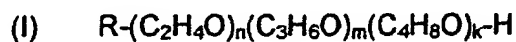
Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9 at different temperatures.

## 5 Detailed Description of Preferred Embodiments

The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of drilling fluids or well service fluids comprising invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing subterranean formations and has particular advantage in applications where the fluids are subjected to low temperatures, as in drilling or in servicing deepwater offshore wells. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and various additives. As the term is used herein, "invert emulsion" or "oil-in-water emulsion" is understood to mean the liquid portion of the drilling fluid comprising an emulsion (excluding solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

In the method of this invention, a composition or compound having the following formula (I) is added to the invert emulsion or oil-based drilling fluid (or well service fluid) to reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity at low temperatures. The compound may be added to the fluid during initial preparation of the fluid or later as the fluid is being used for drilling or well service purposes in the formation. The quantity added is an effective amount to maintain or effect the desired viscosity of the drilling fluid. For purposes of this invention, an "effective amount" of thinner of formula (I) is preferably from about 0.5 to about 15 pounds per barrel of drilling fluid or mud. A more preferred amount of thinner ranges from about 1 to about 5 pounds per barrel of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid.

Formula (I) is:



where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. Preferably, R has about 8 to about 18 carbon atoms; more preferably, R has about 12 to about 18 carbon atoms; and most preferably, R has about 12 to about 14 carbon atoms. Also, most preferably, R is saturated and linear.

The compositions or compounds of formula (I) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides. Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (I), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one molecule of the alkoxyated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n, m, and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (I) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow, such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (I) must contain at least one ethoxy group. Preferably, the compound of formula I will also contain at least one propoxy group ( $C_3H_7O-$ ) or butoxy group ( $C_4H_9O-$ ). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (I) will have a value for m ranging from about 1 to about 10 with k zero or a value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

5 Other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 2 to about 5, and m being about 3 or about 4 with k zero. It is particularly advantageous to  
10 establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (I) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula (I) above will have alkyl radicals containing about 12 to about 18 carbon atoms,  
15 or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Used as thinners according to the method of the invention, the compounds of formula (I) reduce the viscosity or lower the yield point of the drilling fluid to which they are added. These thinners are particularly effective  
20 at low temperatures, i.e., temperatures at or below about 50°F (about 10°C) and most particularly effective at temperatures at or below about 40°F (about 4°C). The lower limit of effectiveness for these thinners is about 14°F (about -10°C). The thinners do not significantly influence or affect the rheology of drilling fluids at high temperatures, particularly temperatures ranging from about  
25 100 to about 250° F or more.

The compounds of formula (I) are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Example drilling fluids comprising invert (water-in-oil) emulsions of  
30 particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and

polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at  
 5 temperatures above about 32°F (about 0°C) or at least as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

10

- (a) most preferably, carboxylic esters of the formula:



15

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 5 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 22 carbon atoms;

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;
- (c) water-insoluble symmetric or asymmetric ethers of monohydric  
 20 alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;
- (d) water-insoluble alcohols of the formula:



25

where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis;  
 30 European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic

diesters). Carboxylic esters of formula (II) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

- 5 In a preferred embodiment of this invention, compounds of formula (I) are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (II) where the radical R' in formula (II) is an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms).
- 10 Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.
- 15 For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters
- 20 disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50 % by volume of one or more

25 preferred compounds (a) - (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the drilling fluids used

30 in the invention, and preferably in amounts not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, thinners of formula (I) are added to drilling fluids comprising invert emulsions containing about 15 to about 35% by volume water and more

preferably 20% by volume water and about 80% by volume oil phase. To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts and/or sodium salts.  $\text{CaCl}_2$  in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) in the range of about 10 to about 60 cP, and preferably in the range of about 15 to about 40 cP, and yield point (YP) in the range of about 5 to about 40 lb/100 ft<sup>2</sup>, and preferably in the range of about 10 to about 25 lb/100 ft<sup>2</sup>, at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft<sup>2</sup>, and should preferably be in the range of about 10 to about 65 lb/100 ft<sup>2</sup>, more preferably about 15 to about 45 lb/100 ft<sup>2</sup>, and most preferably less than about 35 lb/100 ft<sup>2</sup>. A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft<sup>2</sup>.

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA), incorporated herein by reference.

The solids content (not including low gravity solids), or the amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase the density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO<sub>2</sub> and H<sub>2</sub>S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids range from  
5 about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize invert emulsions of the  
10 drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added.  
15 Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

Although the invention has primarily been described in the context of a  
20 method of using compounds of formula (I) as thinners for drilling fluids at low temperatures, the compounds of formula (I) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids at low temperatures.

Further description and use of the invention is shown by the following  
25 examples:

### Examples

To show the effect of the invention, the following experiments were  
30 conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

---

Ester	bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl <sub>2</sub> x 2 H <sub>2</sub> O	lb	27.2
Barite	lb	314.0
Dispersing auxiliary	lb	0.5

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Thinner	lb/bbl	2.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid  
 5 Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and with a C<sub>12/14</sub> fatty alcohol sulfate + 2 EO, sodium salt (C2), with a C<sub>12</sub> ether sulfate, sodium salt (C3) and with an oleic acid sulfonate disodium salt (C4), respectively, as prior art thinners, and comparison was made with these  
 10 thinners and with compounds of formula (I) in accordance with the invention. The formula (I) compounds used for this purpose were as follows:

- |    |    |  |
|----|----|--|
|    | E1 | C12/C14 fatty alcohol containing 2 EO and 4 PO |
|    | E2 | C12/C14 fatty alcohol containing 5 EO and 4 PO |
| 15 | E3 | C12/C18 fatty alcohol containing 5 EO and 4 PO |
|    | E4 | C12/C14 fatty alcohol containing 6 EO and 4 PO |

The invert muds were prepared in a conventional manner and subsequently, at 40°F and 122°F, the rheological characteristics of plastic  
 20 viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.



Measurements E5, E6 and E7 were carried out using the thinners E1, E2 and E4, but in contrast to the details above, 45 lb of solids (rev dust, i.e., filter ash) were also added to each of the muds, in order to demonstrate the advantageous action of the compounds of formula (I) used in accordance with the invention in the case of high solids loading of the emulsions. In these cases, the measurements were taken only after 16 hours of aging at 150°F. The thinner was not added to the muds E5 to E7 until after aging.

The results of the measurements are given in Tables 1a and 1b below.

HALB016

Table 1a

	C1	C1	C2	C2	C3	C3	C4	C4	E1	E2	E2	E3	E3	E4	E4
Temp. °F	40	122	40	122	40	122	40	122	40	122	40	122	40	122	122
PV (cP)	94	28	105	30	n.m.	33	91	24	93	87	28	94	28	83	29
YP lb/100 ft <sup>2</sup>	68	29	71	35	n.m.	62	69	20	70	34	33	62	41	30	30
Gels 10"/10'	27/29	12/13	24/29	15/15	n.m.	26/31	25/25	6/7	25/28	17/19	11/13	14/16	20/24	17/18	13/14

n.m.: not measurable

Table 1b - Measurements with addition of 45 lb rev dust

	C1	C1	E5	E5	E6	E6	E7	E7
Temperature °F	40	122	40	122	40	122	40	122
PV (cP)	94	28	107	37	108	40	108	37
YP lb/100 ft <sup>2</sup>	68	29	37	23	72	42	46	30
Gels 10"/10'	27/29	12/13	12/14	7/9	26/30	14/18	17/19	12/14

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the compounds of formula (I) used in the method and in the emulsions of the invention, especially at low temperatures, in comparison to the prior art. The higher plastic viscosity for E5 to E7 is attributable to the higher proportion of solids in the mud systems.

Further experiments may be seen in Tables 2 to 9. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. This illustrates particularly well the advantageous influence of the compounds of formula (I) on the rheology at low temperatures (40°F, 4°C) without any marked influence at high temperatures (120°F, 50°C). The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 9:

PETROFREE LV® is 2-ethylhexyl octanoate (from Cognis, Germany)

PETROFREE LE® is linear alpha-olefin (from Cognis, Germany)

PETROFREE® is C8-14 fatty acid 2-ethylhexyl ester (from Cognis, Germany)

GELTONE II® is organophilic bentonite (from Baroid, Houston, Texas)

Thinner E1 is Formula I C12/C14 fatty alcohol of the invention containing 2 EO and 4 PO

Thinner E2 is Formula I C12/C14 fatty alcohol of the invention containing 5 EO and 4PO

Table 2

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids					
E2, lb/bbl	0		3		5	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	113	34	107	35
Yield point, lb/100ft <sup>2</sup>	38	14	25	14	19	13
10 sec gel, lb/100ft <sup>2</sup>	16	6	10	6	6	6
10 min gel, lb/100ft <sup>2</sup>	22	11	13	8	9	8
Fann 35 dial readings						
600 rpm	274	94	251	82	233	83
300 rpm	156	54	138	48	126	48
200 rpm	114	40	97	35	88	35
100 rpm	70	25	56	22	49	22
6 rpm	17	6	10	7	7	6
3 rpm	14	5	7	6	5	5

Table 3

5

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	126	50
Yield point, lb/100ft <sup>2</sup>	230	152	19	125
10 sec gel, lb/100ft <sup>2</sup>	108	64	10	50
10 min gel, lb/100ft <sup>2</sup>	110	66	13	52
Fann 35 dial readings				
600 rpm	590	254	271	225
300 rpm	410	203	145	175
200 rpm	336	179	103	149
100 rpm	248	146	59	119
6 rpm	112	79	10	62
3 rpm	100	70	8	58

Table 4

Mud system	PETROFREE LV			
Mud weight, lb/gal	16.0			
Oil/water ratio	80/20			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	152	51	142	40
Yield point, lb/100ft <sup>2</sup>	62	27	40	19
10 sec gel, lb/100ft <sup>2</sup>	22	10	18	10
10 min gel, lb/100ft <sup>2</sup>	48	26	22	12
Fann 35 dial readings				
600 rpm	366	129	324	99
300 rpm	214	78	182	59
200 rpm	158	59	130	45
100 rpm	98	38	78	30
6 rpm	24	11	16	10
3 rpm	20	9	12	9

Table 5

5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	88	29
Yield point, lb/100ft <sup>2</sup>	54	53	37	53
10 sec gel, lb/100ft <sup>2</sup>	33	23	13	26
10 min gel, lb/100ft <sup>2</sup>	38	27	17	30
Fann 35 dial readings				
600 rpm	318	115	213	111
300 rpm	186	84	125	82
200 rpm	139	71	90	70
100 rpm	91	54	56	55
6 rpm	35	25	15	28
3 rpm	32	21	13	25

Table 6

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	113	34
Yield point, lb/100ft <sup>2</sup>	90	47	73	44
10 sec gel, lb/100ft <sup>2</sup>	38	21	27	20
10 min gel, lb/100ft <sup>2</sup>	44	24	30	22
Fann 35 dial readings				
600 rpm	310	115	299	112
300 rpm	200	81	186	78
200 rpm	157	67	142	64
100 rpm	110	50	95	48
6 rpm	42	23	31	22
3 rpm	38	21	27	19

5

Table 7

Mud system	PETROFREE LE			
Mud weight, lb/gal	16.4			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	173	40	107	43
Yield point, lb/100ft <sup>2</sup>	21	9	18	7
10 sec gel, lb/100ft <sup>2</sup>	16	8	11	8
10 min gel, lb/100ft <sup>2</sup>	19	11	15	11
Fann 35 dial readings				
600 rpm	367	89	232	93
300 rpm	194	49	125	50
200 rpm	135	35	88	37
100 rpm	74	22	50	22
6 rpm	12	5	9	6
3 rpm	10	4	7	5

Table 8

Mud system	PETROFREE LE			
Mud weight, lb/gal	11.6			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	80	31	56	32
Yield point, lb/100ft <sup>2</sup>	25	18	27	16
10 sec gel, lb/100ft <sup>2</sup>	12	8	17	9
10 min gel, lb/100ft <sup>2</sup>	20	11	23	11
Fann 35 dial readings				
600 rpm	185	80	139	80
300 rpm	105	49	83	48
200 rpm	77	37	63	37
100 rpm	46	24	43	24
6 rpm	11	7	14	8
3 rpm	9	6	13	7

Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	113	35
Yield point, lb/100ft <sup>2</sup>	38	14	41	16
10 sec gel, lb/100ft <sup>2</sup>	16	6	16	9
10 min gel, lb/100ft <sup>2</sup>	22	11	20	11
Fann 35 dial readings				
600 rpm	274	94	267	86
300 rpm	156	54	154	51
200 rpm	114	40	114	39
100 rpm	70	25	71	26
6 rpm	17	6	18	8
3 rpm	14	5	14	8

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described composition and method can be made without departing from the intended scope of this invention as defined by the appended claims.

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We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said drilling fluid or well service fluid a compound having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

2. The method of claim 1 wherein in said formula, k is zero and m is a number ranging from about 1 to about 10, or m is zero and k is a number ranging from about 1 to about 10.

3. The method of claim 1 wherein in said formula, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

4. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures at least as low as about 40 degrees Fahrenheit.

5. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures above about 32 degrees Fahrenheit.

6. The method of claim 5 wherein said oil phase comprises compounds or compositions selected from the group comprising:

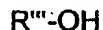
- (f) carboxylic esters of the formula:



where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (g) linear or branched olefins having about 8 to about 30 carbon atoms;  
(h) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (i) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

- (j) carbonic diesters.

7. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said drilling fluid or well service fluid.

8. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said drilling fluid or well service fluid at temperatures less than about 50 degrees Fahrenheit.

9. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said drilling fluid or well service fluid.

10. The method of claim 1 wherein said compound reduces the viscosity of said

drilling fluid or well service fluid at low temperatures.

11. The method of claim 10 wherein said compound does not significantly affect the viscosity of said fluid at high temperatures.

12. The method of claim 1 wherein said compound is added to said fluid when said fluid is prepared.

13. The method of claim 1 wherein said compound is added to said fluid while said fluid is circulating in a wellbore.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and a compound having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15. The drilling fluid or well service fluid of claim 14 wherein said compound is added in sufficient amounts to reduce the viscosity of said fluid at low temperatures.

16. The drilling fluid or well service fluid of claim 14 having a density of from about 8 to about 18 lbs/gal.

17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft<sup>2</sup> at about 40°F.

5 18. A method of reducing the viscosity of an invert emulsion drilling fluid or well service fluid at low temperatures comprising adding to said fluid an effective amount of compound having the formula:



10 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15 19. The method of claim 18 wherein said compound does not significantly affect the viscosity of the drilling fluid at high temperatures.

20 20. The method of claim 18 further comprising circulating said fluid in a wellbore and adding said compound to said fluid during said circulation.

21 21. The method of claim 18 further comprising preparing said fluid and adding said compound to said fluid during said preparation.

25

**Abstract**

A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said  
 5 drilling fluids or well service fluids a thinner having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having  
 10 about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

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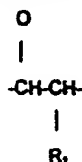
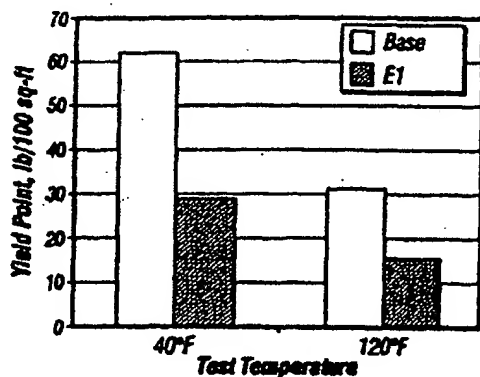
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(I)



(II)

carbon atoms.

(57) Abstract: A method of reducing the viscosity of invert emulsions and oil-based drilling fluids and well service fluids comprising such emulsions over a broad temperature range is disclosed. The method comprises adding to said invert emulsions of the invention a non-ionic surfactant alone or in combination with a co-thinner having the formula:  $R''-(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k-H$  where  $R''$  is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms,  $n$  is a number ranging from about 1 to about 10,  $m$  is a number ranging from about 0 to about 10, and  $k$  is a number ranging from about 0 to about 10. The non-ionic surfactant is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with  $C_{10-22}$  carboxylic acids or  $C_{10-22}$  carboxylic acid derivatives containing at least in position 9/10 and/or 13/14 structural units of general formula (I) where  $R_1$  is a hydrogen atom or an OH group or a group  $OR_2$ .  $R_2$  is an alkyl group of about 1 to about 18 carbon atoms, an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):  $R_3$  is a hydrogen atom, an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of 2 to 21

PCT

## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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<input type="checkbox"/> This person is also inventor.	
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☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

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This person is:

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This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

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## THINNERS FOR INVERT EMULSIONS

### Background of the Invention

#### 1. Field of the Invention

5        This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids over a broad temperature range.

#### 10    2. Description of Relevant Art

      A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill  
15    bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

      A drilling fluid typically comprises water and/or oil or synthetic oil or other  
20    synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in the fluid. Such dispersed water in oil is generally referred to as an invert  
25    emulsion or water-in-oil emulsion.

      A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or fluid-loss control agents, viscosifiers or viscosity control agents, and alkali.  
30    Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

5 An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling  
10 operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

Thinners may be added to the drilling fluid or drilling mud systems before  
15 and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, their effectiveness as thinners is not always uniform over the entire range of  
20 temperatures (typically as low as about 40°F (or lower) to as high as about 250°F (or higher)) at which drilling fluids are used.

Thinners and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further,  
25 drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore, such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising  
30 invert (water-in-oil) emulsions, which are capable of being used over a broad range of temperatures. As used herein, unless indicated otherwise, a "broad

temperature range" shall be understood to generally mean temperatures ranging from about 14°F to about 350°F and preferably ranging from about 40°F to about 250°F.

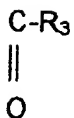
## 5 Summary of the Invention

According to the method of the present invention, at least one compound or composition is added to a water-in-oil or invert emulsion, or a drilling fluid or well service fluid comprising such emulsion, which reduces the viscosity of the emulsion over a broad temperature range or which enables or enhances the ability of the emulsion to maintain its viscosity over a broad temperature range. The compound or composition, which may be generally called a "thinner," continues to have this effect in a drilling fluid or well service fluid comprising the emulsion for use in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations, over a broad temperature range.

The first such thinner compound of the present invention is a non-ionic surfactant which is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives containing at least one double bond in position 9/10 and/or 13/14 having units of the general formula:



where R<sub>1</sub> is a hydrogen atom or an OH group or a group OR<sub>2</sub>, where R<sub>2</sub> is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms or a group of the formula:



- 5 where  $R_3$  is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of about 2 to about 21 carbon atoms.

This first thinner compound may be used alone or may be used in combination with a second or other thinner or "co-thinner" compound having the following formula:

10



- where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

The invention also comprises an invert emulsion drilling fluid or well service fluid containing this first thinner compound, or containing said first thinner compound in combination with said second thinner compound.

20

#### **Brief Description of the Drawings**

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2.

- Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5.

- Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8.

5        Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9.

Figure 9 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 10.

10       Figure 10 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 11.

Figure 11 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 12.

Figure 12 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 13.

15       Figure 13 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 14.

Figure 14 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 15.

20       Figure 15 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 16.

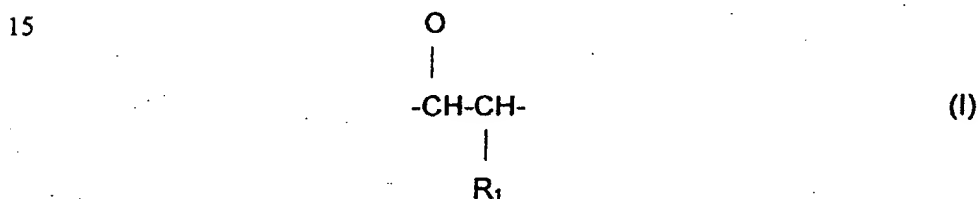
Figure 16 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 17.

#### **Detailed Description of Preferred Embodiments**

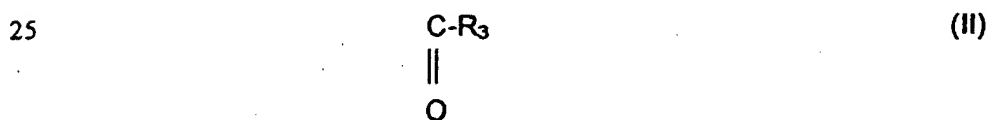
25       The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of invert (water-in-oil) emulsions and drilling fluids or well service fluids comprising such invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing subterranean formations. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water  
30       dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and various additives. As the term is used herein,

an "invert emulsion" or an "oil-in-water emulsion" is understood to mean the liquid portion of a drilling fluid comprising an emulsion (excluding any solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

- 5 In the method of this invention, certain non-ionic surfactants are added to the invert emulsion or oil based drilling fluid (or well service fluid) to "thin" or reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity over a broad range of temperatures. The particular non-ionic surfactants are reaction products of ethylene oxide, propylene oxide and/or butylene oxide with C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub>  
10 carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 (and preferably one or two double bonds in position 9/10 and/or 13/14) having structural units of the general formula (I)



- 20 where R<sub>1</sub> is a hydrogen atom, or an OH group, or a group OR<sub>2</sub>. R<sub>2</sub> is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II)



- 30 R<sub>3</sub> is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

The alkoxylation products may be prepared in accordance with the teaching of DE 39 23 394, which is incorporated herein by reference, by reacting the OH-containing carboxylic acid derivatives, for example, with

ethylene oxide, propylene oxide and/or butylene oxide in the presence of an appropriate catalyst at temperatures between about 110 and about 200°C and pressures between about  $10^5$  Pa and about  $2 \times 10^6$  Pa.

- Suitable starting materials for OH-containing  $C_{10-22}$  carboxylic acids or
- 5  $C_{10-22}$  carboxylic acid derivatives are unsaturated, naturally occurring and/or synthesizable  $C_{10-22}$  carboxylic acids or derivatives thereof containing carboxylic acid radicals having at least one or two double bonds in position 9, 10, 13 and/or 14. Examples of such unsaturated carboxylic acid derivatives are 9-dodecenoic acid, 9-tetradecenoic acid, 9-hexadecenoic acid, 9-octadecenoic
- 10 acid, 9-octadecenoic acid, 9,12-octadecadienoic acid, 9,12,15-octadecatrienoic acid, 9-icosenoic acid, 13-docosenoic acid, and mixtures containing a large amount (i.e., preferably at least about 60%) of such unsaturated carboxylic acids. As starting materials it is preferable to use carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9
- 15 and/or 13 or carboxylic acid mixtures containing at least a large amount (i.e., preferably at least about 80%) of carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9 and/or 13.

- Further examples of suitable unsaturated carboxylic acid derivatives for use in preparing thinner compounds for use in the invention are unsaturated
- 20  $C_{10-22}$  carboxylic esters, such as for example, unsaturated  $C_{10-22}$  carboxylic acid alkyl esters with monohydric alcohols having about 1 to about 18 carbon atoms. Particularly appropriate are  $C_{10-22}$  carboxylic mono-, di- and/or triglycerides containing unsaturated  $C_{10-22}$  carboxylic acid radicals having at least one or two double bonds in position 9 and/or 13. Also suitable are esters of  $C_{10-22}$
- 25 carboxylic acids with other polyols, such as for example ethylene glycol or trimethylolpropane.

- Unsaturated  $C_{10-22}$  carboxylic acid  $C_{1-18}$  alkyl esters are obtainable by esterifying the corresponding unsaturated carboxylic acid or by transesterifying the corresponding mono-, di- and/or triglycerides with  $C_{1-18}$  alkyl alcohols, such
- 30 as, for example, methanol, ethanol, propanol, butanol, isobutanol, 2-ethylhexanol, decanol and/or stearyl alcohol. Examples of such unsaturated



C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl esters are methyl palmitate, methyl oleate, ethyl oleate, isobutyl oleate, 2-ethylhexyl oleate and/or dodecyl oleate and/or C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl ester mixtures containing at least a large fraction (i.e., at least about 60%) of those C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl esters whose carboxylic acid radicals have at least one or two double bonds in position 9 and/or 13, such as, for example, palm oil methyl ester, soya oil methyl ester, colza oil methyl ester and/or tallow fatty acid ethyl ester. Other suitable starting materials for preparing the alkoxylation products for use in the invention are fats and oils of natural origin whose carboxylic acid content is comprised predominantly of unsaturated C<sub>10-22</sub> carboxylic acids having at least one or two double bonds in position 9 and/or 13, such as, for example, olive oil, linseed oil, sunflower oil, soya oil, groundnut oil, cottonseed oil, colza oil, palm oil, lard and tallow.

Unsaturated C<sub>10-22</sub> carboxylic acids and/or C<sub>10-22</sub> carboxylic acid derivatives may be epoxidized to the OH-containing compounds, for example, by reaction with peracetic acid in the presence of acidic catalysts or with performic acid formed *in situ* from formic acid and hydrogen peroxide. The oxirane rings of the epoxidized carboxylic acids and/or carboxylic acid derivatives are subsequently cleaved open to form hydroxyl groups by reaction with hydrogen or protic compounds, such as water, straight-chain and/or branched-chain alkyl and/or alkenyl alcohols having about 1 to about 18 carbon atoms or straight-chain and/or branched-chain, saturated and/or unsaturated C<sub>1-18</sub> carboxylic acids. Other natural or synthetic compounds comprising epoxide-containing carboxylic acids or carboxylic acid derivatives, such as castor oil or hydrogenated castor oil, may also be used. The cleavage conditions are chosen such that the acid-derivative groups and acid groups present remain intact.

The reaction of epoxidized carboxylic acid derivatives and/or epoxidized carboxylic acids with protic compounds may be carried out, for example, in accordance with the processes described in DE 39 23 394.

The carboxylic acids and/or carboxylic acid derivatives obtained by cleaving the oxirane rings, containing carboxylic acid radicals having at least one OH group in position 9, 10, 13 and/or 14, are subsequently reacted by known industrial processes with ethylene oxide, propylene oxide and/or butylene oxide (preferably with ethylene oxide and/or propylene oxide).

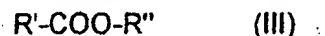
Alkoxylation products obtained by alkoxyating compounds of the formula (I) in which  $R_1$  is a group  $OR_2$  and  $R_2$  is a radical of the formula (II) are preferred. Compounds where the radical  $R_3$  is an alkyl group of about 8 to about 16 carbon atoms, most preferably about 8 to about 10 carbon atoms, are also preferred.

Some non-ionic surfactant compounds that could possibly be used as thinners in accordance with the present invention are also described in WO98/19043 of Henkel Kommandiegesellschaft auf Aktien. That international application teaches use of the compounds in the oil and gas industry as cleaning agents, in contrast to the use of the present invention.

Used as thinners according to the method of the invention, the non-ionic surfactants of the present invention reduce the viscosity or lower the yield point of the drilling fluid to which they are added over a broad range of temperatures.

Example drilling fluids comprising invert (water-in-oil) emulsions of particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at temperatures above about 32°F (about 0°C) or as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

- (a) most preferably, carboxylic esters of the formula:

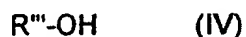


where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;

- (c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (d) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms; and

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis; European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic diesters). Carboxylic esters of formula (III) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

In a preferred embodiment of this invention, non-ionic surfactants of the invention are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (III) where the radical R' in formula (III) is

an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms). Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.

For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50% by volume of one or more preferred compounds (a) – (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the emulsions of the drilling fluids used in the invention in amounts preferably not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, the nonionic surfactant thinners of the present invention are added to drilling fluids (preferably comprising invert emulsions) containing about 15% to about 35% by volume water and more preferably about 20% by volume water and about 80% by volume oil phase.

To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts

and/or sodium salts.  $\text{CaCl}_2$  in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) preferably in the range of about 10 to about 60 cP, and more preferably in the range of about 15 to about 40 cP, and yield point (YP) preferably in the range of about 5 to about 40 lb/100 ft<sup>2</sup>, and more preferably in the range of about 10 to about 25 lb/100 ft<sup>2</sup>, when measured at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft<sup>2</sup>, and should preferably be in the range of about 10 to about 65 lb/100 ft<sup>2</sup>, more preferably about 15 to about 45 lb/100 ft<sup>2</sup>, and most preferably less than about 35 lb/100 ft<sup>2</sup>. A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft<sup>2</sup>.

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA) and Aberdeen, Scotland, incorporated herein by reference.

The solids content (not including low gravity solids), or amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly. Barite and barium sulfate are examples of commonly used weighting agents.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO<sub>2</sub> and H<sub>2</sub>S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids may range  
 5 from about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize invert emulsions  
 10 of the drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S. Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added.  
 15 Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

In an alternative embodiment of the present invention, in addition to the  
 20 non-ionic surfactant thinners of the present invention described above, additional thinners may be added advantageously in combination with said non-ionic surfactant thinners. Such particularly advantageous co-thinners are alkoxyated compounds of the general formula (V):



where R''' is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging  
 30 from about 0 to about 10. Preferably, R''' has about 8 to about 18 carbon atoms; more preferably, R''' has about 12 to about 18 carbon atoms; and most

preferably,  $R'''$  has about 12 to about 14 carbon atoms. Also, most preferably,  $R'''$  is saturated and linear.

The compositions or compounds of formula (V) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding  
5 fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides.  
10 Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (V), the subscripts  $n$  and  $m$  respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one  
15 molecule of the alkoxyated fatty alcohol. The subscript  $k$  indicates the number of butylene oxide (BO) molecules or groups. The subscripts  $n$ ,  $m$ , and  $k$  need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (V) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow,  
20 such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (V) must contain at least one ethoxy group and may have up to or about 10 ethoxy groups. Preferably, the compound of formula (V) will also contain at  
25 least one propoxy group ( $C_3H_6O-$ ) or butoxy group ( $C_4H_8O-$ ). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (V) will have a value for  $m$  ranging from about 1 to about 10 with  $k$  zero or a  
30 value for  $k$  ranging from about 1 to about 10 with  $m$  zero. Most preferably,  $m$  will be about 1 to about 10 and  $k$  will be zero.

Other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 2 to about 5, and  
5 m being about 3 or about 4 with k zero. It is particularly advantageous to establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (V) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula  
10 (V) above will have alkyl radicals containing about 12 to about 18 carbon atoms, or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Both the non-ionic surfactant thinners of the present invention and the thinners of formula (V) may be added to the drilling fluid (or well service fluid)  
15 during initial preparation of the fluid or later as the fluid is being used for drilling or well service purposes in the formation. Alternatively, the non-ionic surfactant thinners may be added first at either of these times and the thinners of formula (V) may be added later. In still another embodiment, the thinners of formula (V) may be added first during either of these times and the non-ionic surfactant  
20 thinners of the invention may be added later.

The quantity of thinners added is an effective amount to maintain or effect the desired viscosity of the drilling fluid, preferably or particularly over a broad temperature range. For purposes of this invention, an "effective amount" of non-ionic surfactant thinner is preferably from about 0.5 to about 15 pounds  
25 per barrel of drilling fluid or mud. A more preferred amount of surfactant thinner ranges from about 1 to about 5 pounds per barrel of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid. When the non-ionic surfactant thinners are used with formula (V) thinners, it is preferred to use the non-ionic surfactant thinners of the present  
30 invention and the thinners of formula (V) in proportions of from about 1:1 to about 10:1.



The thinners of the present invention are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Although the invention has primarily been described in the context of a method of using non-ionic surfactants alone and in combination with the compounds of formula (V) as thinners for drilling fluids over a broad temperature range, these non-ionic surfactants alone and in combination with compounds of formula (V) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids over a broad temperature range.

Further description and use of the invention is shown by the following examples:

#### Examples

To show the effect of the invention, the following experiments were conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

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Ester	Bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl <sub>2</sub> x 2 H <sub>2</sub> O	lb	27.2
Barite	lb	314.0
Rev. dust	lb	45.5
Dispersing auxiliary	lb	0.5

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Thinner	lb/bbl	3.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and  
5 with four non-ionic surfactant thinners E1 to E4 of the invention.

- E1 RS1100™, of Cognis, Germany, see below
- E2 like E1, but reacted with 39 parts of ethylene oxide
- E3 like E1, but reacted with no parts of ethylene oxide
- 10 E4 like E3, but reacted with 25 parts of ethylene oxide
- E5 like E1, but reacted with 50 parts of ethylene oxide

E1 was prepared according to the procedure described in U.S. Patent NO. 5,237,080 to Dante et al., assigned to Henkel Kommandiengesellschaft auf  
15 Aktien, by reacting fatty acids (60% C<sub>8</sub>, 35% C<sub>10</sub>, AN = 361.9) with soya oil epoxide and distilling the product to obtain a clear yellow polyol (viscosity = 5550 mPas; 20°C; OHN = 105, SN = 236, AN = 3.1). This reaction product was then admixed with potassium hydroxide in methanol and heated, after which all traces of methanol were removed. The product was then reacted with  
20 61 parts of ethylene oxide at a pressure not exceeding 5 bar to yield, after neutralization, a clear yellow liquid (OHN = 54.7). This product may be obtained from Cognis, Germany, under the tradename RS 1100.

The invert drilling fluids or muds were prepared in a conventional manner and subsequently, at 40°F and 120°F, the rheological characteristics of  
25 plastic viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

The results of the measurements are given in Table 1:

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the non-ionic surfactant thinners used according to the invention.

Further experiments may be seen in Tables 2 to 17. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 17:

PETROFREE LV ®	is 2-ethylhexyl octanoate (Cognis, Germany)
PETROFREE®	is C8-14 fatty acid 2-ethylhexyl ester (Cognis)
GELTONE II®	is organophilic bentonite (Baroid, Houston, Texas)
Thinner E1	is RS 1100™ (Cognis)

Table 2

Mud system	PETROFREE			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
E1, lb/bbl	0		1	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	75	26	78	23
Yield point, lb/100ft <sup>2</sup>	62	31	29	15
10 sec gel, lb/100ft <sup>2</sup>	26	16	23	8
10 min gel, lb/100ft <sup>2</sup>	27	17	23	10
Fann 35 dial readings				
600 rpm	212	83	185	61
300 rpm	137	57	107	38
200 rpm	110	47	79	30
100 rpm	77	36	49	20
6 rpm	30	18	14	9
3 rpm	26	16	11	7

Table 3

5

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E1	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	140	36
Yield point, lb/100ft <sup>2</sup>	230	152	19	8
10 sec gel, lb/100ft <sup>2</sup>	108	64	7	3
10 min gel, lb/100ft <sup>2</sup>	110	66	13	4
Fann 35 dial readings				
600 rpm	590	254	299	80
300 rpm	410	203	159	44
200 rpm	336	179	110	30
100 rpm	248	146	62	18
6 rpm	112	79	8	3
3 rpm	100	70	6	2

Table 4

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	11	34	108	35
Yield point, lb/100ft <sup>2</sup>	90	47	27	7
10 sec gel, lb/100ft <sup>2</sup>	38	21	4	3
10 min gel, lb/100ft <sup>2</sup>	44	24	7	5
Fann 35 dial readings				
600 rpm	310	115	243	77
300 rpm	200	81	135	42
200 rpm	157	67	95	30
100 rpm	110	50	52	17
6 rpm	42	23	7	3
3 rpm	38	21	5	2

5 Table 5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	62	18
Yield point, lb/100ft <sup>2</sup>	54	53	11	3
10 sec gel, lb/100ft <sup>2</sup>	33	23	3	2
10 min gel, lb/100ft <sup>2</sup>	38	27	5	3
Fann 35 dial readings				
600 rpm	318	115	135	39
300 rpm	186	84	73	21
200 rpm	139	71	52	14
100 rpm	91	54	29	9
6 rpm	35	25	4	2
3 rpm	32	21	3	1

Table 6

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	106	45
Yield point, lb/100ft <sup>2</sup>	38	14	32	10
10 sec gel, lb/100ft <sup>2</sup>	16	6	7	3
10 min gel, lb/100ft <sup>2</sup>	22	11	8	5
Fann 35 dial readings				
600 rpm	274	94	244	100
300 rpm	156	54	138	55
200 rpm	114	40	98	39
100 rpm	70	25	55	22
6 rpm	17	6	8	4
3 rpm	14	5	5	3

5

Table 7

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	37	100	31
Yield point, lb/100ft <sup>2</sup>	53	20	15	4
10 sec gel, lb/100ft <sup>2</sup>	20	8	6	3
10 min gel, lb/100ft <sup>2</sup>	30	14	10	5
Fann 35 dial readings				
600 rpm	273	94	215	66
300 rpm	163	57	115	35
200 rpm	124	42	80	25
100 rpm	80	27	44	15
6 rpm	23	8	7	3
3 rpm	19	7	5	2

Table 8

Mud system	PETROFREE	
Mud weight, lb/gal	9.5	
Oil/water ratio	70/30	
E5, lb/bb	0	3
Temperature, °F	120	120
Plastic viscosity, cP	22	21
Yield point, lb/100ft <sup>2</sup>	39	16
10 sec gel, lb/100ft <sup>2</sup>	16	8
10 min gel, lb/100ft <sup>2</sup>	17	10
Fann 35 dial readings		
600 rpm	83	58
300 rpm	61	37
200 rpm	52	28
100 rpm	40	20
6 rpm	19	8
3 rpm	17	7

5 Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	65	20	52	20
Yield point, lb/100ft <sup>2</sup>	31	33	27	17
10 sec gel, lb/100ft <sup>2</sup>	29	17	17	10
10 min gel, lb/100ft <sup>2</sup>	32	22	26	15
Fann 35 dial readings				
600 rpm	151	73	131	57
300 rpm	96	53	79	37
200 rpm	78	44	66	30
100 rpm	57	34	29	20
6 rpm	29	18	14	9
3 rpm	27	16	12	8

Table 10

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	175	47
Yield point, lb/100ft <sup>2</sup>	230	152	34	10
10 sec gel, lb/100ft <sup>2</sup>	108	64	10	3
10 min gel, lb/100ft <sup>2</sup>	110	66	14	5
Fann 35 dial readings				
600 rpm	590	254	384	104
300 rpm	410	203	209	57
200 rpm	336	179	148	40
100 rpm	248	146	82	23
6 rpm	112	79	12	3
3 rpm	100	70	9	2

5 Table 11

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	106	30
Yield point, lb/100ft <sup>2</sup>	90	47	20	9
10 sec gel, lb/100ft <sup>2</sup>	38	21	8	5
10 min gel, lb/100ft <sup>2</sup>	44	24	11	9
Fann 35 dial readings				
600 rpm	310	115	232	69
300 rpm	200	81	126	39
200 rpm	157	67	88	28
100 rpm	110	50	49	17
6 rpm	42	23	9	5
3 rpm	38	21	7	4



Table 12

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	90	23
Yield point, lb/100ft <sup>2</sup>	54	53	20	9
10 sec gel, lb/100ft <sup>2</sup>	33	23	6	2
10 min gel, lb/100ft <sup>2</sup>	38	27	9	3
Fann 35 dial readings				
600 rpm	318	115	200	55
300 rpm	186	84	110	32
200 rpm	139	71	77	22
100 rpm	91	54	42	13
6 rpm	35	25	6	2
3 rpm	32	21	4	1

Table 13

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E1, lb/bbl	0	1		
E2, lb/bbl	0	2		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	105	33
Yield point, lb/100ft <sup>2</sup>	38	14	15	6
10 sec gel, lb/100ft <sup>2</sup>	16	6	7	3
10 min gel, lb/100ft <sup>2</sup>	22	11	12	6
Fann 35 dial readings				
600 rpm	274	94	225	72
300 rpm	156	54	120	39
200 rpm	114	40	83	28
100 rpm	70	25	45	16
6 rpm	17	6	7	3
3 rpm	14	5	5	2

Table 14

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (5%)					
E2, lb/bbl	0		3		5	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	111	35	114	37
Yield point, lb/100ft <sup>2</sup>	38	14	26	7	17	2
10 sec gel, lb/100ft <sup>2</sup>	16	6	13	5	6	2
10 min gel, lb/100ft <sup>2</sup>	22	11	22	8	9	4
Fann 35 dial readings						
600 rpm	274	94	248	77	245	76
300 rpm	156	54	137	42	131	39
200 rpm	114	40	98	30	91	27
100 rpm	70	25	57	18	50	16
6 rpm	17	6	12	4	6	2
3 rpm	14	5	10	3	4	1

Table 15

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (10%)					
E2, lb/bbl	0		5		7	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	176	59	152	48	150	47
Yield point, lb/100ft <sup>2</sup>	48	19	14	6	20	4
10 sec gel, lb/100ft <sup>2</sup>	16	9	8	6	8	3
10 min gel, lb/100ft <sup>2</sup>	28	17	13	8	10	4
Fann 35 dial readings						
600 rpm	400	137	318	104	320	98
300 rpm	224	78	166	56	170	51
200 rpm	170	57	115	40	118	36
100 rpm	100	34	62	23	64	20
6 rpm	18	8	8	4	8	3
3 rpm	14	7	7	3	6	2

Table 16

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft <sup>2</sup>	38	14	35	14
10 sec gel, lb/100ft <sup>2</sup>	16	6	25	6
10 min gel, lb/100ft <sup>2</sup>	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

Table 17

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft <sup>2</sup>	38	14	35	14
10 sec gel, lb/100ft <sup>2</sup>	16	6	25	6
10 min gel, lb/100ft <sup>2</sup>	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described compositions and method can be made without departing from the intended scope of this invention as defined by the appended claims.

We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said fluid at least one non-ionic surfactant, said surfactant being the reaction product of at least one oxide, selected from the group comprising ethylene oxide, propylene oxide and butylene oxide, with C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



where R<sub>1</sub> is a hydrogen atom, or an OH group, or a group OR<sub>2</sub> and where R<sub>2</sub> is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



- and where R<sub>3</sub> is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

2. The method of claim 1 wherein said non-ionic surfactant comprises alkylation products obtained by reacting C<sub>12-22</sub> carboxylic mono-, di- or triglycerides containing structural units of the formula (I) in at least one position 9, 10, 13, or 14 with at least one oxide of the group comprising ethylene oxide, propylene oxide, and butylene oxide.

3. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures  
5 at least as low as about 40 degrees Fahrenheit.

4. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures  
10 above about 32 degrees Fahrenheit.

5. The method of claim 3 wherein said oil phase comprises compounds or compositions selected from the group comprising:

(a) carboxylic esters of the formula:

15 
$$R'-COO-R''$$

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

20 (b) linear or branched olefins having about 8 to about 30 carbon atoms;

(c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

(d) water-insoluble alcohols of the formula:

25 
$$R'''-OH$$

where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

(e) carbonic diesters.

30 6. The method of claim 5 wherein said oil phase comprises esters wherein the radical R' is an alkyl radical having about 5 to about 21 carbon atoms.

7. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said emulsion.

5 8. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said emulsion.

9. The method of claim 1 wherein said surfactant is added to said drilling  
10 fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said emulsion.

10. The method of claim 1 further comprising adding to said drilling fluid or well service fluid a co-thinner compound having the formula:

15



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about  
20 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

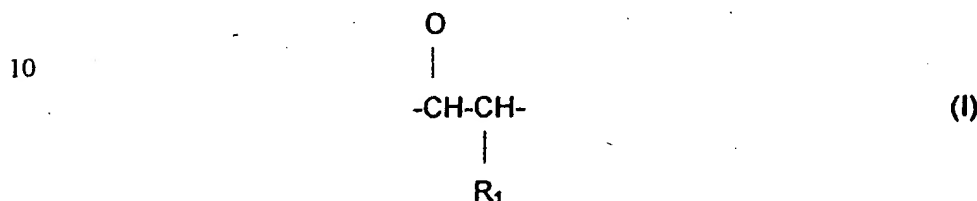
11. The method of claim 10 wherein in said formula for said co-thinner compound, k is zero and m is a number ranging from about 1 to about 10, or m is  
25 zero and k is a number ranging from about 1 to about 10.

12. The method of claim 10 wherein in said formula for said co-thinner compound, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

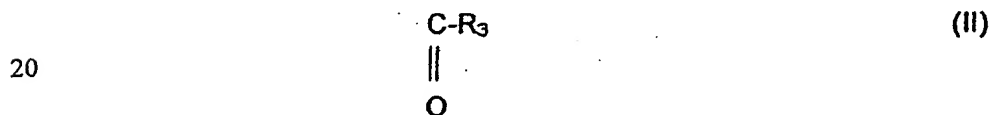
30

13. The method of claim 10 wherein said surfactant and said co-thinner compound are added in proportions ranging from about 1:1 to about 10:1.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and at least one non-ionic surfactant, said surfactant being the reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



- 15 where R<sub>1</sub> is a hydrogen atom, or an OH group, or a group OR<sub>2</sub>, and where R<sub>2</sub> is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



where R<sub>3</sub> is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

15. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added in sufficient amounts to reduce the viscosity of said fluid.
16. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added to said fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said surfactant per barrel of said fluid.
17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft<sup>2</sup> at about 40°F.



18. The drilling fluid or well service fluid of claim 14 further comprising a compound having the formula:



5

where R''' is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

10

19. The drilling fluid or well service fluid of claim 18 wherein said surfactant and said compound are in proportions ranging from about 1:1 to about 10:1.

20. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid during preparation of said fluid or after such fluid has begun service in the wellbore.

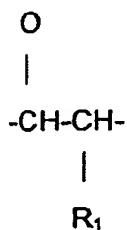
21. The method of claim 10 wherein said co-thinner compound is added to said fluid during preparation of said fluid or after said fluid has begun service in the wellbore.

**Abstract**

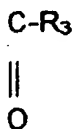
A method of reducing the viscosity of invert emulsions and oil-based drilling fluids and well service fluids comprising such emulsions over a broad temperature range is disclosed. The method comprises adding to said invert emulsions of the invention a non-ionic surfactant alone or in combination with a co-thinner having the formula:



- where  $R'''$  is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms,  $n$  is a number ranging from about 1 to about 10,  $m$  is a number ranging from about 0 to about 10, and  $k$  is a number ranging from about 0 to about 10. The non-ionic surfactant is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with  $C_{10-22}$  carboxylic acids or  $C_{10-22}$  carboxylic acid derivatives containing at least in position 9/10 and/or 13/14 structural units of the general formula:



where  $R_1$  is a hydrogen atom or an OH group or a group  $OR_2$ .  $R_2$  is an alkyl group of about 1 to about 18 carbon atoms, an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula:



$R_3$  is a hydrogen atom, an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of 2 to 21 carbon atoms.

IN THE UNITED STATES DISTRICT COURT  
FOR THE EASTERN DISTRICT OF TEXAS  
TYLER DIVISION

HALLIBURTON ENERGY SERVICES, INC.,

Plaintiff,

v.

M-I, LLC,

Defendant.

CIVIL ACTION NO. 6:05 CV 155

JURY DEMANDED

**M-I, LLC'S MOTION FOR LEAVE TO ADD  
INEQUITABLE CONDUCT DEFENSE TO ITS PLEADINGS**

Defendant M-I, LLC ("M-I") files contemporaneously herewith its First Amended Answer to conform and update its existing defenses to the facts discovered in this case, and also to add an antitrust counterclaim based on information obtained in depositions just completed on January 26, 2006. Such amendment is allowed under the Discovery Order without leave prior to January 27, 2006.

The Discovery Order also provides that after October 28, 2005 it is necessary to file a motion for leave to add inequitable conduct allegations. Accordingly, M-I requests leave to add inequitable conduct allegations.

**I. THE BASIS FOR M-I'S INEQUITABLE CONDUCT ALLEGATIONS**

Halliburton alleges that M-I infringes 88 claims United States Patent No. 6,887,832 (the '832 patent). The '832 patent issued on May 3, 2006. Halliburton filed this lawsuit on the same day. This lawsuit was M-I's first knowledge of the '832 patent. The '832 patent claims a "fragile gel drilling fluid" or a method of using a "fragile gel drilling fluid" comprising an invert emulsion base, one or more thinners, one or emulsifiers, and one or more weighting agents.

Inequitable conduct obtains when a patent applicant or the applicant's representative breaches the duty to prosecute patent applications with candor, good faith, and honesty. Because

of the requirement that inequitable conduct claims be pled with factual specificity, M-I did not include any inequitable conduct allegations in its Answer. None of the facts demonstrating inequitable conduct were evident from the file history.

In August, M-I noticed the deposition of a first named inventor, Kimberly Burrows for September 20, 2005. (Ex. 1.) In mid-September, based on the departure of one of its outside counsel from the Godwin firm, Halliburton requested that M-I postpone the deposition, and that the parties begin exchanging documents in October. M-I agreed. (Ex. 2.) On September 26, 2006, due to the approaching hurricane, Halliburton asked to postpone the deposition for one to two weeks. (Ex. 3.) Ultimately, Halliburton did not provide Ms. Burrows for deposition until October 26, 2006. (Ex. 4.) The delays in this deposition, and in the production of documents by Halliburton, prevented M-I from evaluating any inequitable conduct prior to October 28, 2005. Thereafter, M-I took the deposition of named inventors Don Siems (December 12, 2005), David Carbajal (January 12, 2006)<sup>1</sup> and their representative to the patent office, Karen Tripp (January 26, 2006).

Based on documents and information obtained during those depositions, M-I now has evidence that the applicants for the patent-in-suit or their representatives committed inequitable in the following ways:

1. Applicants disclosed to the patent examiner a brochure on Halliburton's Petrofree and XP-07 formulations, copyright 1997, that notes RM-63 is an additive for these formulations. Applicant's did not disclose Halliburton's own literature that explained "RM-63 alters the fluid structure, producing rapid but *fragile gels*." (Ex. 5.) Two named inventors have admitted that on the face of these publications the claimed inventions of the '832 patent are disclosed.
2. Applicants disclosed in the patent specification a comparison between a Petrofree SF formulation and the patented "fragile gel" drilling fluid, which Halliburton calls

---

<sup>1</sup> Each named inventor has admitted that the combination of an invert emulsion base, one or more thinners, one or emulsifiers, and one or more weighting agents, as claimed was known more than one year before the filing date of the '832 patent.

“Accolade,” without disclosing to the patent examiner that Halliburton’s own tests showed Petrofree LV was admittedly the closest “prior art” with the most properties like Accolade.

3. During prosecution, the patent examiner cited four prior art references, each which disclosed an invert emulsion base, one or more thinners, one or emulsifiers, and one or more weighting agents, to reject all the claims of the ‘832 patent application. Applicants’ representative responded that the cited prior art drilling fluids did not inherently possess the “fragile gel” properties of the claimed invention, yet this was never discussed with the named inventors, and no testing was done to determine if this was a true statement. Accordingly, Applicants’ representative made this statement of fact without any factual basis, with intent to deceive the patent examiner.
4. Applicants also duplicated almost word-for-word a section from a prior art patent, United States Patent No. 6,289,989 (‘the ‘989 patent,’ attached as Ex. 6) into the specification of the ‘832 patent-in-suit as a description of an “appropriate” thinner for use in the claims of ‘832 patent. (Compare Ex. 6 at 3:7-33 and Ex. 7 the ‘832 patent at 10:25-49 and 14:64 – 15:18.) The ‘989 patent was more material than the references cited by the patent examiner because it discloses an invert emulsion base, the exact thinner disclosed in the ‘832 patent, one or emulsifiers, and one or more weighting agents, and thus must result in a “fragile gel” since it has identical ingredients. (Ex. 6 at 7:31-40.) Applicants knowingly withheld this material prior art from the patent examiner.

Inequitable conduct includes affirmative misrepresentations of a material fact, failure to disclose material information, or submission of false material information, coupled with an intent to deceive. *Baxter Int’l, Inc. v. McGaw, Inc.*, 149 F.3d 1321, 1327 (Fed. Cir. 1998). The actions and omissions described above constitute inequitable conduct, and are the basis for that allegation in M-I’s First Amended Answer.

FED. R. CIV. P. 15(a) provides that leave to amend “shall be freely given when justice so requires.” The Supreme Court has stated that “this mandate is to be heeded.” *Foman v. Davis*, 371 U.S. 178, 182 (1962). While the trial court has discretion to determine whether amendments will be allowed, the Fifth Circuit cautions that:

“Discretion” may be a misleading term, for rule 15(a) severely restricts the judge’s freedom, directing that leave to amend ‘shall be freely given when justice so requires.’ It evinces a bias in favor of granting leave to amend. The policy of the federal rules is to permit liberal amendment to facilitate determination of

claims on the merits and to prevent litigation from becoming a technical exercise in the fine points of pleading.

*Dussouy v. Gulf Coast Investment Corp.*, 660 F.2d 594, 597-598 (5th Cir. 1981). M-I thus seeks leave to amend.

## II. CONCLUSION

M-I established the factual basis for its allegations of inequitable conduct through documents produced or otherwise obtained after the deadline to add inequitable conduct allegations, and through depositions of the inventors that occurred after October 28, 2005 (primarily based on Halliburton's requests for delay due to change in Halliburton's outside counsel). M-I thus files the present motion promptly and in good faith, and requests that the Court grant leave to allow M-I to add the defense of inequitable conduct.

Respectfully Submitted,

DATED: January 26, 2006

By /s/ John R. Keville

John R. Keville

SBN 00794085

kevillej@howrey.com

Stephen H. Cagle

cagles@howrey.com

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OF COUNSEL:

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ccapshaw@mailbmc.com

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Longview, Texas 75601

Telephone: (903) 236-9800

Facsimile: (903) 236-8787

ATTORNEYS FOR DEFENDANT

M-I, LLC

**CERTIFICATE OF CONFERENCE**

I hereby certify that I made several attempts to confer with counsel for the Plaintiff and as of the time of filing of this motion I have not been able to discuss this motion with them and cannot state Halliburton's position at this time.

/s/ John R. Keville

**CERTIFICATE OF SERVICE**

I hereby certify that the following counsel of record who are deemed to have consented to electronic service are being served this 26th day of January, 2006, with a copy of M-I, LLC'S MOTION FOR LEAVE TO ADD INEQUITABLE CONDUCT DEFENSE TO ITS PLEADING via the Court's CM/ECF system per Local Rule CV-5(a)(3). Any other counsel of record will be served by, electronic mail, facsimile transmission and/or first class mail on this same date.

Gregory M. Luck  
[gluck@godwinpappas.com](mailto:gluck@godwinpappas.com)  
GODWIN PAPPAS LANGLEY RONQUILLO, LLP  
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Monte M. Bond  
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OF COUNSEL:  
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ATTORNEYS FOR PLAINTIFF,  
HALLIBURTON ENERGY SERVICES, INC.

/s/ John R. Keville



UNITED STATES DISTRICT COURT  
EASTERN DISTRICT OF TEXAS  
TYLER DIVISION

HALLIBURTON ENERGY SERVICES, INC.

Plaintiff,

v.

M-I, LLC

Defendant.

CIVIL ACTION NO. 6:05CV155

**NOTICE OF DEPOSITION OF KIMBERLY BURROWS-LAWSON**

TO: Kimberly Burrows-Lawson, by and through the attorneys for plaintiff, Godwin Gruber, LLP, Renaissance Tower, 1201 Elm Street, Suite 1700, Dallas, TX 75270.

PLEASE TAKE NOTICE that commencing on September 20, 2005 at 9:00 a.m. (or at another date and time agreed to in writing by the parties) at the offices of Howrey, LLP, 1111 Louisiana, 25<sup>th</sup> Floor, Houston, TX 77002, Defendant will take the deposition upon oral examination of Kimberly Burrows-Lawson pursuant to Rule 30 of the Federal Rules of Civil Procedure, before a notary public or duly authorized officer, authorized to administer oaths.

This deposition will continue from day-to-day until completed. The deposition will be videotaped. Your attendance and cross-examination are invited.

Respectfully Submitted,

DATED: August 26, 2005

By 

John R. Keville  
kevillej@howrey.com  
HOWREY, LLP  
1111 Louisiana, 25<sup>th</sup> Floor  
Houston, TX 77002  
Telephone: (713) 787-1400  
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OF COUNSEL:  
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Longview, Texas 75601  
Telephone: (903) 236-9800  
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**CERTIFICATE OF SERVICE**

I certify that a true and correct copy of the foregoing **NOTICE OF DEPOSITION OF KIMBERLY BURROWS-LAWSON** was served by email, facsimile and first class mail on August 26, 2005, on all counsel of record, as follows:

Eric W. Buether  
ebuether@godwingruber.com  
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Dallas, Texas 75270  
(214) 939-4400  
(214) 760-7332 - Facsimile

ATTORNEYS FOR PLAINTIFF,  
HALLIBURTON ENERGY SERVICES, INC.

OF COUNSEL:  
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(903) 593-0846 - Facsimile

A handwritten signature in black ink, appearing to read "Michael E. Jones", written over a horizontal line.

DALLAS HOUSTON

MONTE M. BOND  
Direct Dial: 214.939.4617  
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214 760 7332 Fax

GodwinGruber.com

September 16, 2005

**VIA E-MAIL: kevillej@howrey.com**  
**AND REGULAR MAIL**

John R. Keville  
Howrey LLP  
1111 Louisiana  
25th Floor  
Houston, Texas 77002-5242

Re: *Halliburton Energy Services, Inc. vs. M-I, LLC* – Case No. 06:05CV155

Dear Mr. Keville:

Enclosed please find Plaintiff's Preliminary Infringement Contentions pursuant to Local Patent Rule 3-1 and Plaintiff's Initial Disclosures pursuant to Fed. R. Civ. P. 26(a) and the Court's Discovery Order. Plaintiff's disclosures pursuant to Local Patent Rule 3-2 were transmitted under cover of a separate letter.

Additionally, I am in receipt of your letter to Mr. Luck dated September 15, 2005. Thank you for agreeing to reschedule the deposition of Ms. Burrows-Lawson by a reasonable amount of time. As Mr. Luck explained, the attorneys originally handling this matter for Halliburton recently left the firm and we appreciate your consideration in this regard. We will work with you to reach a mutually agreeable date for the deposition.

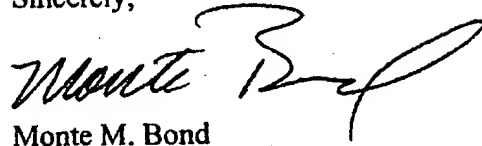
As for document production, we should also be in a position to exchange the documents in "early October" as set forth in your letter. Again we appreciate your consideration in this regard.

As for mediation we do not believe mediation can be productive until both parties have disclosed at least their preliminary positions on the issues involved in the case. MI's initial preliminary contentions under the Local Patent Rules are not due until October 28, 2005. All the dates proposed by you fall before that date. We propose that the mediation take place the week of November 7, 2005. This should give us sufficient time to review MI's disclosures filed on the 28<sup>th</sup>. We will inform Mr. McGowan of our proposal in a response to your letter to him.

Mr. John R. Keville  
September 16, 2005  
Page 2

If you have any questions please do not hesitate to contact me.

Sincerely,



Monte M. Bond

MMB:ss  
Enclosures

cc: Craig Roddy  
William Imwalle  
Greg Luck (w/o enclosures)  
Michael Jones

G O D W I N G R U B E R

Attorneys  
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September 26, 2005

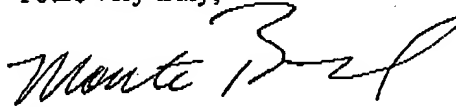
Mr. John R. Keville  
Howrey LLP  
750 Bering Drive  
Houston, Texas 77057-2198

Re: Halliburton Energy Services, Inc. v. M-I, LLC  
Our File No. 50028.0032

Dear John:

In light of the approaching hurricane our witness scheduled for deposition next week, Kimberly Burrows-Lawson, has evacuated to Oklahoma City with her family. She does not know when she will be able to return to the Houston area. In light of these unknown circumstances, I would like to temporarily postpone her deposition which is currently scheduled for next Thursday. As soon as she returns to Houston and is able to take care of her personal matters regarding her family and her home, we will provide you with new deposition dates for her. I do not anticipate this being more than a one to two week delay. I appreciate your cooperation in postponing this deposition for a short time period.

Yours very truly,



Monte Bond

MB:js  
D1206984v1\50028.0032 CORR

**G O D W I N   G R U B E R**

*Attorneys  
A Limited Liability Partnership*

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<b>FAX</b>	Number of Pages (including cover sheet)	2	Date of Transmittal	September 26, 2005

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Client/Matter  
Number: 50028.0034

Comments:

If you do not receive all materials being transmitted, please call Scarlett at 214-939-8614

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GREGORY M. LUCK  
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October 7, 2005

**VIA FACSIMILE**Mr. John R. Keville  
HOWREY, LLP  
1111 Louisiana, 25th Floor  
Houston, TX 77002RE: *Halliburton Energy Services, Inc. v. MI, LLC*; Civil Action No. 5-CV-155

Dear John:

We will produce Kim Burrows-Lawson on Wednesday, October 26, 2005 beginning at 9:00 o'clock a.m. We will produce Ms. Burrows at our offices. Please confirm the scheduling for this deposition so that Ms. Burrows may make plans accordingly.

Very truly yours,

  
Gregory M. Luck

GML/jkn

cc: Monte Bond  
Thomas W. Sankey



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<b>FAX</b>	Number of Pages (including cover sheet)	Date of Transmittal
	2	October 7, 2005

To	Company	Phone	Fax
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From	Gregory M. Luck
Client/Matter Number	Halliburton Energy Services, Inc. v. MI, LLC; Civil Action No. 5-CV-155 50028-0034

Comments      Please note the Revised date of the deposition.

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191821v.1/14375.0002

## Baroid Drilling Fluids Products

### RM-63 Rheology Modifier

RM-63 rheology modifier is a specially formulated product designed to improve rheological and suspension characteristics of oil-based fluids. RM-63 alters the fluid structure, producing rapid but fragile gels and increased low-shear properties. High shear properties (i.e., 600 and 300 rpm values) are relatively unaffected by the RM-63 rheology modifier. It can be applied in a wide range of oil/water ratio fluids and has been applied in BAROID 100™, INVERMUL®, EZ-OIL™, and BAROID 50/50™ systems. By using the RM-63 modifier when drilling with weighted mud in deviated boreholes, the tendency for barite "sag" or settling can be minimized.

RM-63 modifier can be used in conjunction with oil-based fluid viscosifiers (e.g., organo-based clays) to provide the extra suspension and hole cleaning required for horizontal and extended reach drilling. The use of RM-63 modifier has proven more cost effective than the sole use of bentonite-based organo clays for enhancing suspension. It does not significantly increase the plastic viscosity or yield point of the mud. However, significant increases in 6 and 3 rpm viscosities and gel strengths have been noted, and suspension of weighting materials rely on this improved gel structure.

#### Recommended Uses:

- Used in oil-based drilling fluids
- Increases low shear rheological properties
- Reduces barite sag in highly deviated wellbores
- Improves cuttings transport

#### Major Advantages:

- Provides suspension in a wide range of oil/water ratio fluids
- Will not significantly change mud properties other than suspension
- Compatible with all common oil mud additives
- Very cost effective alternative to increasing suspension with organo clays
- Thermally stable to 450°F (232°C)

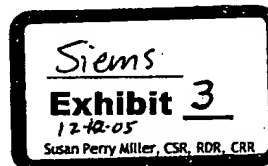
#### Physical Properties:

Appearance	dark amber liquid
Chemical Class	polymeric fatty acid
Specific gravity	0.95
Solubility in water, 68°F (20°C)	none
Solubility in oil	oil dispersible liquid

#### Recommended Treatment:

Used when barite settling is expected, as in deviated or horizontal drilling

Normal treatment	1-3 lb/bbl
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 \*BAROID 50/50, BAROID 100, EZ-OIL, FAST and RM-63 are trademarks of Baroid Technology, Inc.  
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 P.O. Box 1075 Houston, Texas 77240

DMD-64  
 Printed in U.S.A.

**Typical Properties:**

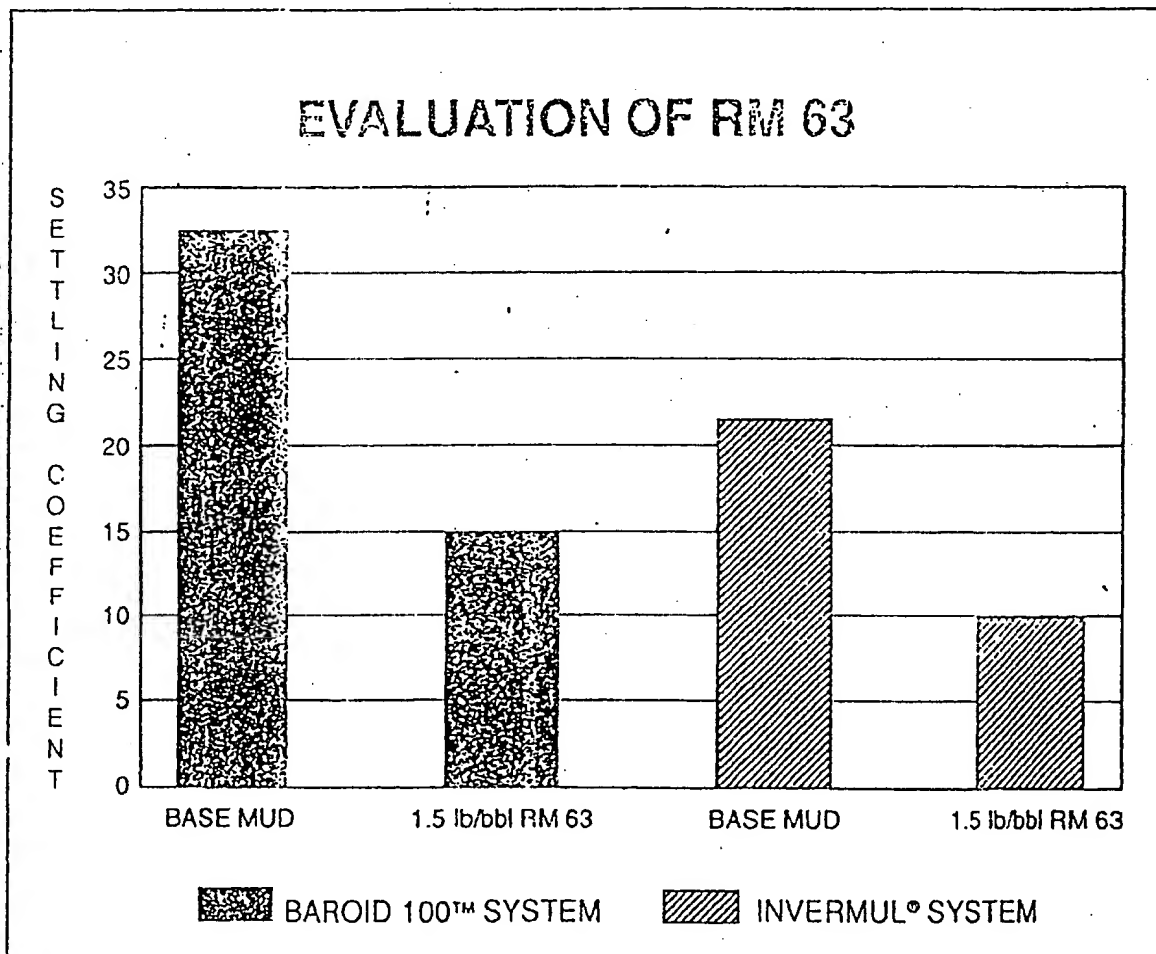
Graph 1 is a representation of improved suspension by only small additions of RM-63. The systems tested were BAROID 100, an oil-oil fluid, and INVERMUL, an invert emulsion. The Settling Coefficient (as determined by the Baroid HAST™ system) indicates the relative barite settling that could be expected of these weighted systems if placed in a deviated borehole. The addition of RM-63 reduced the settling tendency in each case by more than 45%, and did not significantly influence the plastic viscosity or yield point.

**Packaging:**

RM-63 rheology modifier is packaged in non-returnable 55-gallon steel drums containing 435 pounds (197.6 kg).

**Availability:**

RM-63 rheology modifier can be purchased through any Baroid Service Center or through the Baroid Houston Office located at 3000 N. Sam Houston Parkway East, Houston, Texas 77032. The product can be ordered through the Customer Service Department at (713) 987-5067.





US006289989B1

(12) **United States Patent**  
**Mueller et al.**

(10) Patent No.: **US 6,289,989 B1**  
(45) Date of Patent: **Sep. 18, 2001**

(54) **USE OF BIODEGRADABLE ALCOXYLATION PRODUCTS FOR CLEANING BOREHOLES, BORING INSTRUMENTS OR BORINGS**

(75) Inventors: **Helnz Mueller, Monheim; Claus-Peter Herold, Mettmann; Berthold Schreck, Duesseldorf; Stefan Podubrin, Muelheim an der Ruhr; Andreas Heldbreder, Duesseldorf, all of (DE)**

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(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/297,480**

(22) PCT Filed: **Oct. 21, 1997**

(86) PCT No.: **PCT/EP97/05800**

§ 371 Date: **Jul. 2, 1999**

§ 102(c) Date: **Jul. 2, 1999**

(87) PCT Pub. No.: **WO98/19043**

PCT Pub. Date: **May 7, 1998**

(30) **Foreign Application Priority Data**

Oct. 30, 1996 (DE) ..... 196 43 857

(51) Int. Cl.<sup>7</sup> ..... **E21B 37/00**

(52) U.S. Cl. .... **166/311; 507/266; 507/267**

(58) Field of Search ..... **166/311, 312; 510/108, 109, 413, 421, 475, 476; 507/266, 267, 930, 931**

(56) **References Cited**

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0 386 636	9/1990 (EP)
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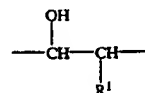
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(74) Attorney, Agent, or Firm—John E. Drach; Glenn E. J. Murphy; Henry E. Millson, Jr.

(57) **ABSTRACT**

A process for cleaning boreholes, drilling equipment and drill cuttings is presented involving the application of a cleaning composition to surfaces and the subsequent removal of the cleaning composition and soils. The cleaning composition contains a cleaning additive having alkoxylation products obtained by the reaction of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof with an OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof, where structural units corresponding to formula (I):



comprise one or both of the 9/10 or 13/14 positions, wherein R<sup>1</sup> is a hydrogen atom, an OH group or a OR<sup>2</sup> group, R<sup>2</sup> is an alkyl group containing 1 to 18 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or a group corresponding to formula (II):



where R<sup>3</sup> is a hydrogen atom, an alkyl group containing 1 to 21 carbon atoms or an alkylene group containing 2 to 21 carbon atoms. The cleaning composition is biodegradable.

**42 Claims, No Drawings**

**MIPI 000157**

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# USE OF BIODEGRADABLE ALKOXYLATION PRODUCTS FOR CLEANING BOREHOLES, BORING INSTRUMENTS OR BORINGS

This application is filed under 35 U.S.C. 371 and based on PCT/EP97/05800, filed October 30, 1996.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to the use of biodegradable alkoxylation products for cleaning boreholes, drilling equipment and drill cuttings, to an additive containing these alkoxylation products, to a cleaning composition containing this additive and to processes for cleaning boreholes, drilling equipment and drill cuttings.

### 2. Discussion of Related Art

In the drilling and development of oil and gas occurrences, cleaning steps have to be introduced at various stages to ensure problem-free drilling and production. Thus, after the actual drilling process, the borehole has to be prepared for the production of oil or gas (completion). To this end, an outer tube or casing has to be introduced and cemented in place to stabilize the borehole. The cement is passed through the casing in an aqueous liquid form, emerges at the lower end of the casing and hardens between the borehole wall and the casing. To guarantee optimal cementing, the borehole wall and the casings have to be freed from adhering residues of the drilling mud and adhering fine-particle solids. If this is not done, the layer of concrete is in danger of developing voids or channels which reduce the stability of the concrete. In addition, residues of the drilling mud and the cement together can form a gelatinous mass which prevents the cement from setting so that the stability of the cement jacket is further reduced.

After the casing has been introduced into the borehole, the actual production tube, which is smaller in diameter than the casing, is installed. In addition, a sealing fluid (or packer fluid as it is also known) is introduced between the production tube and the inner wall of the casing. Before this packer fluid is introduced, the annular space between the casing and the production tube is cleaned. In particular, all fine-particle solids still adhering to the wall of the casing or production tube have to be removed to guarantee the performance of the packer fluid.

The choice of the cleaning composition to perform the functions mentioned above is also determined by the nature of the drilling mud used. In principle, drilling muds are divided into water-based types and oil-based types. Oil-based drilling muds are mainly used today either as so-called "true oil muds", i.e. muds which contain little if any dispersed water, or as so-called invert muds which contain between 5 and 45% by weight of water as dispersed phase, i.e. which form a w/o emulsion. In addition there are water-based o/w emulsions which contain a heterogeneous finely disperse oil phase in a continuous aqueous phase. Petroleum products, such as mineral or diesel oils, are normally used as the oil phase. However, increasingly more stringent ecological requirements have recently led to the development of synthetic oil phases, for example containing esters of certain fatty acids. Drilling muds based on such ester oils are described, for example, in European patents 386 636, 374 671 and 374 672 and show distinctly improved behavior compared with petroleum products in regard to their biological degradability and toxicity. Where drilling muds based on synthetic esters are used, the formation of tacky residues on metal surfaces and on the borehole wall are occasionally observed and can also lead to troublesome deposits.

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In The same way as the cement used for the cementing process, the cleaning compositions are pumped downwards through the drill pipe in liquid form, emerge at the bottom of the borehole and are forced upwards through the annular space between the tube and the borehole wall. They detach residues of the drilling muds and solid particles adhering to the surfaces and remove them from the borehole. One such process is described in detail, for example, in WO 94/29570. The compositions are normally used in the form of aqueous or non-aqueous solutions or dispersions. However, they may also be added to the drilling mud in concentrated, solid or liquid form.

Cleaning compositions for the functions described above may be, for example, mixtures of citric acid, pyrophosphate and potassium salts used in solid or dissolved form. These compositions are suitable both for true oil muds and for invert muds. An alternative method is described in European patent 513 899, according to which a fluid containing a dispersed gas phase is used for cleaning boreholes. Under the temperature and pressure conditions prevailing in the borehole, the gas phase forms gas bubbles of a certain size which lead to a turbulent flow of the fluid pumped through the borehole and thus enable the borehole to be mechanically cleaned.

In oil production, deposits of paraffin or asphalt are often formed in the borehole or on the production tubes and reduce output. These deposits have to be removed in the course of stimulation work in order to improve the production rate.

Various solutions have been proposed in the prior art for removing the above-mentioned residues by suitable cleaning compositions. Thus, WO 96/01358 discloses an additive containing an ether amine and/or a base oil, for example an ester, a diester, a surfactant or an olefin, in combination with an alkyl alcohol, preferably a terpene alcohol. This additive is used in the form of an aqueous mixture. WO 95/17244 describes a composition for cleaning surfaces soiled with oil which contain surfactants with HLB values of at least 8 in combination with an oil. Ethoxylated sorbitan fatty acid esters are mentioned as preferred surfactants.

Now, although compositions based on ethoxylated sorbitan fatty acid esters develop a favorable cleaning effect, particularly against the residues occurring where ester-based drilling muds are used, their biological degradability and toxicity do not meet all the requirements of increasingly more stringent environmental legislation.

Accordingly, the problem addressed by the present invention was to provide cleaning compositions for boreholes, drilling equipment or drill cuttings which would show improved ecological compatibility in relation to known compositions for at least the same cleaning performance.

It has now been found that compositions for cleaning boreholes or drilling equipment which contain certain alkoxylation products obtained by reaction of certain OH-containing C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives with ethylene oxide, propylene oxide and/or butylene oxide are at least comparable in their cleaning performance with the prior art and, at the same time, have improved environmental compatibility.

DE 41 34 973 describes water-based cleaning compositions for hard surfaces which contain between 1.0 and 30% by weight of an alkoxylation product of OH-containing carboxylic acids and/or derivatives thereof with 30 to 85% of ethylene oxide or propylene oxide as nonionic surfactants. However, there is nothing in this document to suggest that the compositions in question would also be suitable for cleaning soiled surfaces which come into contact with

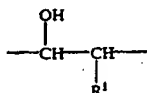
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drilling muds based on petroleum or synthetic esters. In addition, there is nothing in the document in question to indicate that such compounds would be usable under the extreme conditions encountered in oil boreholes in regard to temperature, pressure and exposure to shear forces and aggressive media, such as salt water.

In a first embodiment, the present invention relates to the use of biodegradable alkoxylation products obtained by reaction of ethylene oxide, propylene oxide and/or butylene oxide with C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives which, at least in the 9/10 and/or 13/14 position, contain structural units corresponding to general formula (I):



in which

R<sup>1</sup> is a hydrogen atom or an OH group or a group OR<sup>2</sup>, where R<sup>2</sup> is an alkyl group containing 1 to 18 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or a group corresponding to formula (II):



where R<sup>3</sup> is a hydrogen atom, an alkyl group containing 1 to 21 carbon atoms or an alkylene group containing 2 to 21 carbon atoms, for cleaning boreholes, drilling equipment or drill cuttings.

The alkoxylation products themselves are not new. They may be produced in accordance with the teaching of German patent 39 23 394, which is also part of the disclosure of the present application, by reacting the OH-containing carboxylic acid derivatives with ethylene oxide, propylene oxide and/or butylene oxide in the presence of a suitable catalyst, for example at temperatures of 110 to 200° C. and under pressures of 10<sup>5</sup> to 2x10<sup>6</sup> Pa.

Suitable educts for OH-containing C<sub>10-22</sub> carboxylic acids or C<sub>10-22</sub> carboxylic acid derivatives are any OH-free, unsaturated naturally occurring and/or synthetic C<sub>10-22</sub> carboxylic acids or derivatives which contain carboxylic acid functions with at least one or two double bonds in the 9, 12, 13 or 14 position. Examples of unsaturated carboxylic acid derivatives are 9c-dodecenoic acid, 9c-tetradecenoic acid, 9c-hexadecenoic acid, 9c-octa-decenoic acid, 9t-octadecenoic acid, 9c,12c-octadecadienoic acid, 9c, 12c, 15c-octadecatrenoic acid, 9c-eicosanoic acid and/or 13c-docosenoic acid and/or mixtures with at least a large content of such unsaturated carboxylic acids. Preferred educts are carboxylic acids containing 16 to 22 carbon atoms and at least one or two double bonds in the 9 and/or 13 position or carboxylic acid mixtures with at least a large content of carboxylic acids containing 16 to 22 carbon atoms and at least one or two double bonds in the 9 and/or 13 position.

Suitable unsaturated carboxylic acid derivatives are, for example unsaturated C<sub>10-22</sub> carboxylic acid esters, for example unsaturated C<sub>10-22</sub> carboxylic acid alkyl esters with monohydric alcohols containing 1 to 18 carbon atoms. C<sub>10-22</sub> carboxylic acid mono-, di- and/or triglycerides containing OH-free unsaturated C<sub>10-22</sub> carboxylic acid functions with at least one or two double bonds in the 9 and/or 13

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position are particularly suitable. Esters of C<sub>10-22</sub> carboxylic acids with other polyols, such as ethylene glycol or trimethylol propane, are also suitable.

Examples of unsaturated C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl esters, which can be obtained in known manner by esterification of the corresponding unsaturated carboxylic acid or by transesterification of the corresponding mono-, di- and/or triglycerides with C<sub>1-18</sub> alkyl alcohols, for example methanol, ethanol, propanol, butanol, isobutanol, 2-ethyl hexanol, decanol and/or stearyl alcohol, are palmitoleic acid methyl ester, oleic acid methyl ester, oleic acid ethyl ester, oleic acid isobutyl ester, oleic acid-2-ethyl hexyl ester and/or oleic acid dodecyl ester and/or C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl ester mixtures with at least a high percentage content of such C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl esters, which have at least one or two double bonds in the 9 and/or 13 position in the carboxylic acid esters, such as palm oil methyl ester, soybean oil methyl ester, rapeseed oil methyl ester and/or tallow fatty acid ethyl ester. Other particularly suitable starting materials for the production of the alkoxylation products are fats and/or oils of natural origin of which the carboxylic acid content is made up predominantly of unsaturated C<sub>10-22</sub> carboxylic acids with at least one or two double bonds in the 9 and/or 13 position, such as for example olive oil, linseed oil, sunflower oil, soybean oil, peanut oil, cottonseed oil, rapeseed oil, palm oil, lard and/or tallow.

Unsaturated C<sub>10-22</sub> carboxylic acids and/or C<sub>10-22</sub> carboxylic acid derivatives can be epoxidized to the OH-containing compounds, for example, by reaction with peracetic acid in the presence of acidic catalysts or with performic acid formed in situ from formic acid and hydrogen peroxide. The oxirane rings of the epoxidized carboxylic acids and/or carboxylic acid derivatives are then opened to form hydroxy groups by reaction with hydrogen or protic compounds, such as water, linear and/or branched alkyl and/or alkenyl alcohols containing 1 to 18 carbon atoms or linear and/or branched, saturated and/or unsaturated C<sub>1-18</sub> carboxylic acids. However, other natural or synthetic compounds containing epoxide-containing carboxylic acids or carboxylic acid derivatives, such as castor oil or hydrogenated castor oil, may also be used. The ring opening conditions are selected so that the acid derivative and acid groups present remain intact. The reaction of epoxidized carboxylic acid derivatives and/or epoxidized carboxylic acids with protic compounds may be carried out, for example, by the process described in DE 39 23 394.

The carboxylic acids and/or carboxylic acid derivatives containing carboxylic acid functions with at least one OH group in the 9, 10, 13 and/or 14 position which are obtained by opening of the oxirane rings are then reacted with ethylene oxide, propylene oxide and/or butylene oxide by known industrial processes. The reaction is preferably carried out with ethylene oxide and/or propylene oxide. It is particularly preferred to use alkoxylation products obtained by alkoxylation of compounds corresponding to formula (I), in which R<sup>1</sup> is a group OR<sup>2</sup> where R<sup>2</sup> is a group corresponding to formula (II). Compounds in which R<sup>3</sup> is an alkyl group containing 8 to 16 carbon atoms and preferably 8 to 10 carbon atoms are particularly preferred.

The alkoxylation products are used in particular for cleaning boreholes. More particularly, the walls of the borehole itself or even production tubes or casing walls can be cleaned using the alkoxylation products. Drilling equipment in the context of the invention includes, for example, pipelines and tools which are used in drilling operations and which come into contact with other drilling

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muds and/or crude oil. In addition, the alkoxylation products may also be used for cleaning drill cuttings. Drill cuttings accumulate during the drilling process and, in the case of offshore drilling, have to be dumped on the seabed in the vicinity of the drilling platform which can lead to the large-scale introduction of mineral oil into the environment. In order largely to avoid ecological damage to the sea, the cuttings are cleaned and freed from residues of the drilling mud before dumping.

Alkoxylation products obtained by reaction of mono-, di- or triglycerides of the  $C_{10-22}$  carboxylic acids with ethylene oxide, propylene oxide and/or butylene oxide are preferably used. The alkoxylation products are preferably obtained by addition of 0.2 to 4 parts of ethylene oxide, propylene oxide and/or butylene oxide with 1 part of the OH-containing  $C_{10-22}$  carboxylic acids and/or  $C_{10-22}$  carboxylic acid derivatives. Alkoxylation products obtained by addition of 1.0 to 2.0 parts and, more particularly, 1.5 to 1.8 parts of ethylene oxide, propylene oxide and/or butylene oxide with 1 part of the OH-containing  $C_{10-22}$  carboxylic acids and/or  $C_{10-22}$  carboxylic acid derivatives are particularly preferred. Products obtained by reaction with ethylene oxide and/or propylene oxide are particularly suitable. It can be of particular advantage to use products obtained by reaction solely with ethylene oxide or solely with propylene oxide.

It is of advantage to use the alkoxylation products in the form of a mixture with certain alcohols. These mixtures may be directly added to a stimulation fluid. However, they are preferably formulated together with additional ingredients to form cleaning compositions which are used for cleaning boreholes, drilling equipment or drill cuttings.

Accordingly, the present invention also relates to additives for cleaning boreholes, drilling equipment or drill cuttings which contain the biodegradable alkoxylation products described above in quantities of 40 to 90% by weight and  $C_{1-10}$  alcohols in quantities of 10 to 60% by weight. In addition, the additives preferably contain 1 to 10% by weight of water.

The alcohols may be branched or unbranched, saturated or unsaturated. Alcohols equivalent in their ecological compatibility to the alkoxylation products mentioned above are preferred. Suitable alcohols are, for example, ethanol, hexanol, octanol, methyl hexanol, 2-Ethyl hexanol and butyl glycol are particularly preferred. However, other compounds which have a high flashpoint, preferably terpenes and/or terpene alcohols, may also be used. Limonene is particularly preferred.

In addition, the additives contain esters of  $C_{1-24}$  fatty acids with  $C_{1-18}$  alcohols. Suitable alcohols also include polyols, such as ethylene glycol, glycerol or trimethylol propane. Esters of  $C_{2-12}$  alcohols with  $C_{18-24}$  fatty acids, C4-12 fatty acids and  $C_{12-16}$  fatty acids are preferred. The additives advantageously contain mixtures of these esters with 2-ethyl hexanol or butyl glycol, preferably in a ratio by weight of 2:1 to 1:2 and more preferably in a ratio of 1:1. Additives such as these are particularly suitable for cleaning soil of high oil content or as oil spill dispersants. In the latter case, crude oil floating on the surface of water is sprayed with the compositions so that the oil is dispersed into fine droplets which undergo more rapid biological degradation. Conventional surfactants have hitherto been used for this purpose although they have higher aquatic toxicity than the alkoxylation products present in the compositions according to the invention because the known surfactants greatly reduce surface tension.

The additives are preferably formulated as solutions or dispersions, compositions containing salt water being pre-

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ferred. However, other suitable solvents may also be used. Accordingly, the invention also relates to compositions for cleaning boreholes, drilling equipment or drill cuttings which contain the additives described above dissolved or dispersed in seawater or highly concentrated salt solutions.

Seawater in the context of the present invention is water with a salt content of 0.2 to 5% by weight (cf. Rompps Chemie-Lexikon, 9th Edition 1992, pages 2669-2670). The compositions may contain the additives in quantities of 1 to 90% by weight although compositions containing the additives in quantities of 1 to 10% by weight, based on the composition as a whole, are preferred. Besides the additives according to the invention, the compositions may contain other suitable ingredients, such as emulsifiers or thickeners, for example polymers or carboxymethyl cellulose, fluid loss additives or weighting agents, such as barite. The compositions according to the invention are particularly suitable for cleaning boreholes where ester-based water-containing invert muds have been used. The compositions may also be used with advantage in boreholes which are to be prepared for cementing or where the annular space between the casing and production tube is to be filled with a packer fluid. Not only metal surfaces, such as the surfaces of drill pipes and casings, but also and in particular the walls of oil boreholes can be cleaned with the compositions according to the invention.

The compositions according to the invention may be used in all cleaning processes known to the expert which are involved in geological drilling both offshore and on land. These cleaning processes include, in particular, the removal of paraffin deposits from borehole walls. Boreholes are normally cleaned by a cleaning fluid being pumped under pressure through the borehole and the deposits being removed from the walls of the borehole by the cleaning fluid. The deposits are transported from the borehole with the fluid. Accordingly, the present invention also relates to a process for cleaning boreholes in which one of the compositions according to the invention is pumped through the borehole by the method described above.

The compositions may also be used for cleaning preferably oil-covered articles, such as tools, pipelines or drill cuttings which accumulate in geological drilling. To this end, the composition according to the invention is sprayed onto or applied to the surfaces of the articles or the articles to be cleaned are immersed in the compositions. The oil and other soil types are thus removed from the surfaces. The surfaces are then contacted with water so that the compositions are removed with the soils. For example, the surfaces are sprayed with a jet of water.

Accordingly, the present invention also relates to a process for cleaning the surfaces of drilling equipment or drill cuttings in which the surfaces are first contacted with a cleaning fluid and are then sprayed with water, one of the compositions according to the invention described above being used as the cleaning fluid.

#### EXAMPLES

To determine the cleaning performance of borehole cleaning compositions, three different compounds are diluted with seawater to form solutions containing 5% by weight of an additive. These additives contain (based on the weight of the additives) 56% by weight of 2-ethyl hexanol, 1% by weight of water and 45% by weight of

A sorbitan monooleate+10 EO (OMC 809, a product of Henkel KGaA)

B sorbitan monooleate+20 EO (Tween 20, a product of Atlas)

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C reaction product of a hydrogenated soybean oil epoxide with 61% by weight EO reacted with head-fractionated fatty acid. Component C was prepared by heating 1225 g (7.9 moles) of head-fractionated fatty acid (60% C<sub>8</sub>, 35% C<sub>10</sub>, acid value 361.9) with stirring to 150° C. and adding 1770 g (7.5 moles, based on epoxide oxygen) of soybean oil epoxide (epoxide oxygen=6.78) over a period of 1 hour. After the addition, the temperature was slowly increased to 170° C., followed after 2 hours (epoxide oxygen <0.15%) by distillation in vacuo up to 200° C. (469 g distillate). The end product is a yellow clear polyol (viscosity 5550 mPas; 20° C.; OH value 105, saponification value 236, acid value 3.1).

After the addition of 6.9 g of a 30% solution of potassium hydroxide in methanol, 423 g (39 parts) of the reaction product of soybean oil epoxide with head-fractionated fatty acid were heated in an autoclave to 100° C. At this temperature, the traces of methanol present were removed by 5x evacuation and purging with nitrogen as inert gas. After the reaction temperature had been raised to 150° C., a total of 660 g (61 parts) of ethylene oxide was added in portions in such a way that the pressure in the reactor did not exceed 5 bar. After the reaction, the temperature was reduced to 80-100° C. and, to remove traces of ethylene oxide, a vacuum was applied for about 15 minutes and the reaction mixture was neutralized with lactic acid. The crude product is a clear yellow liquid (OH value 54.7).

The soil used was an invert drilling mud which had been conventionally prepared using the following ingredients:

250 ml	2-ethyl hexyl oleate
83.5 g	water
42.6 g	organophilic bentonite
1.2 g	lime
9.7 g	w/o emulsifier ("EZ-Mul" of NL Baroid)
100.0 g	CaCO <sub>3</sub>
100.0 g	barite
26.8 g	CaCl <sub>2</sub> ·2H <sub>2</sub> O
42.6 g	organophilic lignite ("Duratone" of NL Baroid)

The plastic viscosity (PV), yield point (YP) and gel strength after 10 seconds and 10 minutes were first determined by viscosity measurements at 50° C. before ageing. The invert mud was then aged for 16 h at 200° F. in a roller oven and the viscosity values were remeasured at 50° C.

The following results were obtained:

	Before Ageing	After Ageing
Plastic viscosity (PV) [cP]	175	130
Yield point (YP) [lb/200 ft <sup>2</sup> ]	128	95
Gel strength [lb/100 ft <sup>2</sup> ]		
10 seconds	31	51
10 minutes	27	30

Using a brush, 8 g of the aged drilling mud were uniformly applied to the walls of a mixing beaker of known weight up to the 350 ml mark. 200 ml of the 5% by weight cleaning solution were then poured into the mixing beaker which was then shaken by hand for 3 minutes. The solution was then poured out and the mixing beaker was placed upside down, i.e. with its opening underneath, on a filter paper for 2 minutes. The mixing beaker was then weighed. The percentage cleaning effect could be determined from the difference in relation to the known weight of the mixing

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beaker and the drilling mud. The beaker was then reshaken for 3 minutes with the previously used solution. The mixing beaker was then reweighed after it had been placed upside down on a filter paper for another 2 minutes.

The percentage cleaning performance of the individual compositions is shown in Table 1.

TABLE 1

Composition	% Cleaning Performance 1st Cleaning Step	% Cleaning Performance 2nd Cleaning Step
A	0	38.2
B	0.5	20.2
C	28.6	38.9

The test results show that the biodegradable compositions (C) according to the invention are comparable in their cleaning performance on oil-covered surfaces with the hitherto known, ecologically unsafe compounds based on ethoxylated sorbitan monofatty acid esters (A and B), but by comparison develop a distinct cleaning effect in only the first cleaning step. Accordingly, the alkoxylation products according to the invention act more quickly than the comparison products.

The biological degradability of the alkoxylation product used in composition (C) was determined by OECD method 301 A (die-away test). It was found that 54% of the DOC (dissolved organic carbon) could not be detected after 28 days.

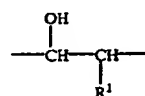
The EC<sub>50</sub> for the same substance is 800 mg/l (daphnia test, acute toxicity as measured in accordance with EU Guideline 92/69/EEC, 31st July, 1992)

The LC<sub>50</sub> is 220 mg/l (zebra fish test, acute toxicity as measured in accordance with EU Guideline 92/169/EEC, 31st July, 1992).

What is claimed is:

1. A process for cleaning boreholes, drilling equipment and drill cuttings comprising:

(a) forming a cleaning additive comprising at least one alkoxylation product obtained by the reaction of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof with an OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof, wherein structural units corresponding to formula (I):



comprise one or both of the 9/10 or 13/14 positions, wherein R<sup>1</sup> is a hydrogen atom, an OH group or a OR<sup>2</sup> group, R<sup>2</sup> is an alkyl group containing 1 to 18 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or a group corresponding to formula (II):



wherein R<sup>3</sup> is a hydrogen atom, an alkyl group containing 1 to 21 carbon atoms or an alkylene group containing 2 to 21 carbon atoms; and

(b) contacting the surface of a borehole, drilling equipment or drill cuttings with the cleaning additive.

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2. The process of claim 1 wherein the cleaning additive is formed by the reaction of ethylene oxide, propylene oxide or butylene oxide with a mono-, di- or triglyceride of C<sub>10-22</sub> carboxylic acid.

3. The process of claim 1 wherein the carboxylic acid or the carboxylic acid in the derivative thereof contains 16 to 22 carbon atoms.

4. The process of claim 1 wherein the carboxylic acid or the carboxylic acid in the derivative thereof comprises a C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl ester.

5. The process of claim 1 wherein the cleaning additive is formed by reacting 0.2 to 4 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

6. The process of claim 5 wherein the cleaning additive is formed by reacting 1.0 to 2.0 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

7. The process of claim 6 wherein the cleaning additive is formed by reacting 1.5 to 1.8 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

8. The process of claim 1 wherein the cleaning additive further comprises a C<sub>1-10</sub> alcohol.

9. The process of claim 8 wherein said alcohol is 2-ethyl hexanol or butyl glycol.

10. The process of claim 1 wherein the cleaning additive further comprises 1 to 10 percent water.

11. The process of claim 1 further comprising dissolving or dispersing the cleaning additive in seawater.

12. The process of claim 1 wherein the cleaning additive is present at 1 to 90 percent by weight in a cleaning composition, based on the composition as a whole.

13. The process of claim 12 wherein the cleaning additive is present at 1 to 10% by weight in a cleaning composition, based on the composition as a whole.

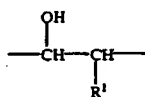
14. The process of claim 1 comprising pumping the cleaning additive through a borehole under pressure.

15. The process of claim 1 comprising applying the cleaning additive to a surface by spraying or immersion.

16. The process of claim 15 further comprising rinsing said surface with water to remove the cleaning additive.

17. A process for cleaning boreholes, drilling equipment and drill cuttings comprising:

- (a) forming a cleaning additive comprising
  - (i) from 10 to 60 percent by weight of at least one C<sub>1-10</sub> alkyl alcohol; and
  - (ii) from 40 to 90 percent by weight of at least one alkoxylation product obtained by the reaction of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof with an OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof, wherein structural units corresponding to formula (I):



comprise one or both of the 9/10 or 13/14 positions, wherein R<sup>1</sup> is a hydrogen atom, an OH group or a OR<sup>2</sup> group, R<sup>2</sup> is an alkyl group containing 1 to 18 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms, or a group corresponding to formula (II):

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(II)

wherein R<sup>3</sup> is a hydrogen atom, an alkyl group containing 1 to 21 carbon atoms or an alkylene group containing 2 to 21 carbon atoms, and

(b) contacting the surface of a borehole, drilling equipment or drill cuttings with the cleaning additive.

18. The process of claim 17 wherein the at least one alkoxylation product is formed by the reaction of ethylene oxide, propylene oxide or butylene oxide with a mono-, di- or triglyceride of C<sub>10-22</sub> carboxylic acid.

19. The process of claim 17 wherein the carboxylic acid or the carboxylic acid in the derivative thereof in (ii) contains 16 to 22 carbon atoms.

20. The process of claim 17 wherein the carboxylic acid or the carboxylic acid in the derivative thereof in (ii) comprises a C<sub>10-22</sub> carboxylic acid C<sub>1-18</sub> alkyl ester.

21. The process of claim 17 wherein the at least one alkoxylation product formed by reacting 0.2 to 4 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

22. The process of claim 21 wherein the at least one alkoxylation product is formed by reacting 1.0 to 2.0 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

23. The process of claim 22 wherein the at least one alkoxylation product is formed by reacting 1.5 to 1.8 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof.

24. The process of claim 17 wherein (i) is 2-ethyl hexanol or butyl glycol.

25. The process of claim 17 wherein the cleaning additive further comprises 1 to 10 percent water.

26. The process of claim 17 further comprising dissolving or dispersing the cleaning additive in seawater.

27. The process of claim 17 wherein the cleaning additive is present at 1 to 90 percent by weight in a cleaning composition, based on the composition as a whole.

28. The process of claim 27 wherein the cleaning additive is present at 1 to 10% by weight in a cleaning composition, based on the composition as a whole.

29. The process of claim 17 comprising pumping the cleaning additive through a borehole under pressure.

30. The process of claim 17 comprising applying the cleaning additive to a surface by spraying or immersion.

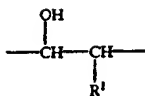
31. A process for cleaning boreholes, drilling equipment and drill cuttings comprising:

- (a) forming a cleaning additive comprising
  - (i) at least one alkoxylation product obtained by the reaction of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof with an OH-containing C<sub>10-22</sub> carboxylic acid or derivative thereof, wherein structural units corresponding to formula (I):

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comprise one or both of the 9/10 or 13/14 positions, wherein  $R^1$  is a hydrogen atom, an OH group or a  $OR^2$  group,  $R^2$  is an alkyl group containing 1 to 18 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or a group corresponding to formula (II):



wherein  $R^3$  is a hydrogen atom, an alkyl group containing 1 to 21 carbon atoms or an alkylene group containing 2 to 21 carbon atoms, and

(ii) at least one ester of a  $C_{1-24}$  fatty acid with a  $C_{1-18}$  alcohol; and

(b) contacting the surface of a borehole, drilling equipment or drill cuttings with the cleaning additive.

32. The process of claim 31 wherein the at least one alkoxylation product is formed by the reaction of ethylene oxide, propylene oxide or butylene oxide with a mono-, di- or triglyceride of  $C_{10-22}$  carboxylic acid.

33. The process of claim 31 wherein the carboxylic acid or the carboxylic acid in the derivative thereof in (ii) contains 16 to 22 carbon atoms.

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(i) 34. The process of claim 31 wherein the carboxylic acid or the carboxylic acid in the derivative thereof in (ii) comprises a  $C_{10-22}$  carboxylic acid  $C_{1-18}$  alkyl ester.

5 35. The process of claim 31 wherein the at least one alkoxylation product is formed by reacting 0.2 to 4 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing  $C_{10-22}$  carboxylic acid or derivative thereof.

36. The process of claim 35 wherein the at least one alkoxylation product formed by reacting 1.0 to 2.0 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing  $C_{10-22}$  carboxylic acid or derivative thereof.

15 37. The process of claim 36 wherein the at least one alkoxylation product is formed by reacting 1.5 to 1.8 moles of ethylene oxide, propylene oxide or butylene oxide with 1 mole of OH-containing  $C_{10-22}$  carboxylic acid or derivative thereof.

20 38. The process of claim 37 wherein the cleaning additive is present at 1 to 10% by weight in a cleaning composition, based on the composition as a whole.

39. The process of claim 31 comprising pumping the cleaning additive through a borehole under pressure.

40. The process of claim 31 comprising applying the cleaning additive to a surface by spraying or immersion.

41. The process of claim 31 wherein (ii) is at least one ester of a  $C_{2-12}$  alcohol with a  $C_{18-24}$  fatty acid.

42. The process of claim 31 wherein (ii) is at least one ester of a  $C_{4-12}$  fatty acid or a  $C_{12-16}$  fatty acid and a  $C_{2-12}$  alcohol.

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